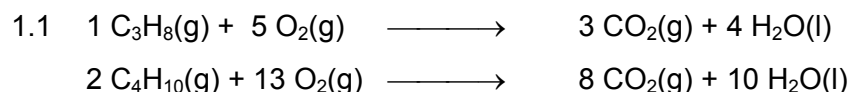


Worked Solutions to the Problems

Solution problem 1: Combustion Energy



1.2 Combustion energy (reaction enthalpy): $\Delta_c H^0 = \sum_p \Delta_f H^0(p) - \sum_r \Delta_f H^0(r)$

$$\Delta_c H^0(\text{propane}) = 3 \cdot (-393.5 \text{ kJ mol}^{-1}) + 4 \cdot (-285.8 \text{ kJ mol}^{-1}) - (-103.8 \text{ kJ mol}^{-1})$$

$$\Delta_c H^0(\text{propane}) = -2220 \text{ kJ mol}^{-1}$$

$$\Delta_c H^0(\text{butane}) = 4 \cdot (-393.5 \text{ kJ mol}^{-1}) + 5 \cdot (-285.8 \text{ kJ mol}^{-1}) - (-125.7 \text{ kJ mol}^{-1})$$

$$\Delta_c H^0(\text{butane}) = -2877 \text{ kJ mol}^{-1}$$

- 1.3 On the assumption that oxygen and nitrogen behave like ideal gases, the volume is proportional to the molar amount:

$$n_{\text{N}_2} = n_{\text{O}_2} \frac{V_{\text{N}_2}}{V_{\text{O}_2}} = n_{\text{O}_2} \cdot 3.76.$$

5 mol of O₂ and 18.8 mol of N₂ are needed for the burning of 1 mol of propane.

6.5 mol of O₂ and 24.4 mol of N₂ are needed for the burning of 1 mol of butane.

When $V = n \cdot R \cdot T \cdot p^{-1}$, the volumes of air are:

propane: $V_{\text{air}} = (5 + 18.8) \text{ mol} \cdot 8.314 \text{ J (K mol)}^{-1} \cdot 298.15 \text{ K} \cdot (1.013 \cdot 10^5 \text{ Pa})^{-1}$
 $V_{\text{air}} = 0.582 \text{ m}^3$

butane: $V_{\text{air}} = (6.5 + 24.4) \text{ mol} \cdot 8.314 \text{ J (K mol)}^{-1} \cdot 298.15 \text{ K} \cdot (1.013 \cdot 10^5 \text{ Pa})^{-1}$
 $V_{\text{air}} = 0.756 \text{ m}^3$

- 1.4 Under these circumstances, water is no longer liquid but gaseous. The combustion energies change due to the enthalpy of vaporization of water and higher temperature of the products.

Energy of vaporization of water at 25°C:

$$\Delta_v H^0(\text{H}_2\text{O}) = \Delta_f H^0(\text{H}_2\text{O}(\text{l})) - \Delta_f H^0(\text{H}_2\text{O}(\text{g})) = -285.8 \text{ kJ mol}^{-1} - (-241.8 \text{ kJ mol}^{-1})$$

$$\Delta_v H^0(\text{H}_2\text{O}) = 44 \text{ kJ mol}^{-1}$$

The energy needed to increase the temperature of the products up to 100°C is:

$$\Delta H(T) = (T - T^0) \sum_i n_i C_p(i)$$

The energy E released by burning of 1 mol of gas is:

$$E(\text{propane}, T) = (-2220 + 4 \cdot 44) \text{ kJ} + (T - T^0) (3 \cdot 37.1 + 4 \cdot 33.6 + 18.8 \text{ mol} \cdot 29.1) \text{ JK}^{-1}$$

$$E(\text{propane}, T) = -2044 \text{ kJ} + (T - T^0) \cdot 792.8 \text{ JK}^{-1} \quad (1)$$

$$E(\text{propane}, 373.15 \text{ K}) = -1984.5 \text{ kJ mol}^{-1}.$$

$$E(\text{butane}, T) = (-2877 + 5 \cdot 44) \text{ kJ} + (T - T^0) (4 \cdot 37.1 + 5 \cdot 33.6 + 24.4 \text{ mol} \cdot 29.1) \text{ JK}^{-1}$$

$$E(\text{butane}, T) = -2657 \text{ kJ} + (T - T^0) \cdot 1026.4 \text{ JK}^{-1} \quad (2)$$

$$E(\text{butane}, 373.15 \text{ K}) = -2580.0 \text{ kJ mol}^{-1}.$$

1.5 Efficiency of propane: $\eta_{\text{propane}} = \frac{E(\text{propane}, 373.15 \text{ K})}{\Delta_c H^0} = 1984.5/2220 = 89.4\%$.

$$\eta_{\text{butane}} = \frac{E(\text{butane}, 373.15 \text{ K})}{\Delta_c H^0} = 2580.0/2877 = 89.7\%.$$

The energy is stored in the thermal energies of the products.

1.6. The combustion energies have been calculated in 1.4., equation (1), (2):

$$E(\text{propane}, T) = -2044 \text{ kJ} + (T - T^0) \cdot 792.8 \text{ J K}^{-1}$$

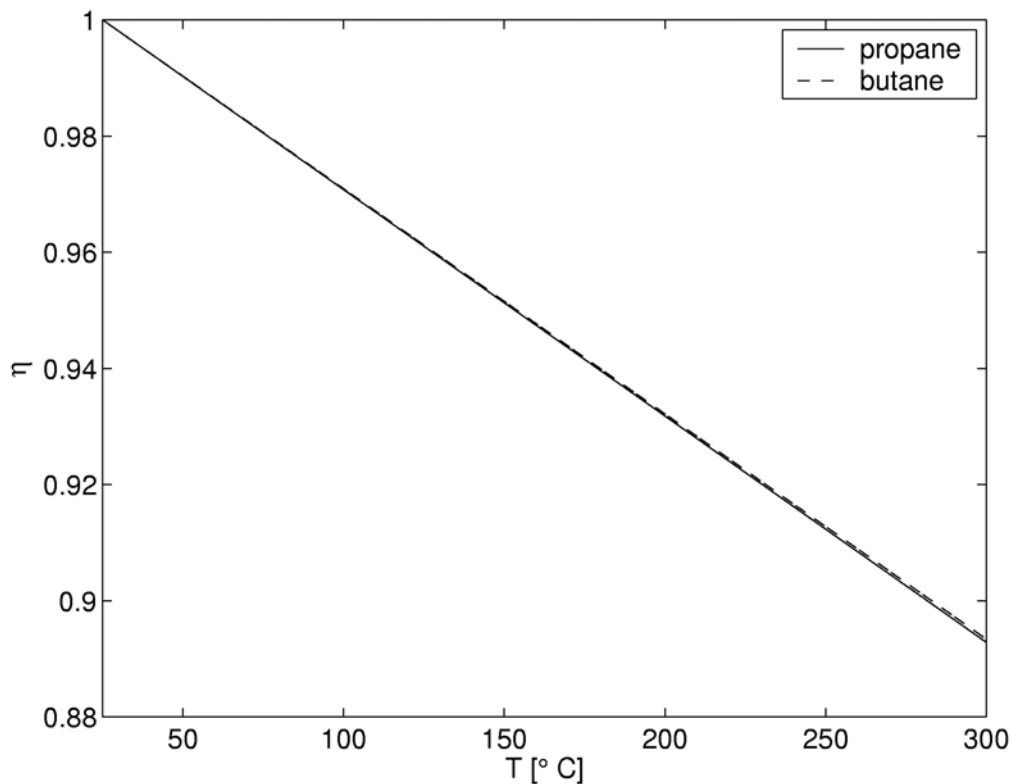
$$E(\text{butane}, T) = -2657 \text{ kJ} + (T - T^0) \cdot 1026.4 \text{ J K}^{-1}$$

the efficiencies are given by:

$$\text{Propane: } \eta_{\text{propane}}(T) = 1 - 3.879 \cdot 10^{-4} \cdot (T - T^0)$$

$$\text{Butane: } \eta_{\text{butane}}(T) = 1 - 3.863 \cdot 10^{-4} \cdot (T - T^0)$$

The plot shows that there is really no difference between the efficiencies of burning propane and butane.



1.7 $n_j = \rho_j \frac{V_j}{M_j}$

$$n_{\text{propane}} = 0.493 \text{ g cm}^{-3} \cdot 1000 \text{ cm}^3 \cdot (44.1 \text{ g mol}^{-1})^{-1} = 11.18 \text{ mol}$$

$$n_{\text{butane}} = 0.573 \text{ g cm}^{-3} \cdot 1000 \text{ cm}^3 \cdot (58.1 \text{ g mol}^{-1})^{-1} = 9.86 \text{ mol}$$

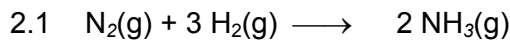
$$E_i = n_i \cdot E(\text{propane/butane}, 373.15\text{K})$$

$$E_{\text{propane}} = 11.18 \text{ mol} \cdot (-1984.5 \text{ kJ mol}^{-1}) = -22.19 \text{ MJ}$$

$$E_{\text{butane}} = 9.86 \text{ mol} \cdot (-2580.0 \text{ kJ mol}^{-1}) = -25.44 \text{ MJ}$$

Despite the fact that there is less butane per volume, the energy stored in 1 L of butane is higher than the energy stored in 1 L of propane.

Solution problem 2: Haber-Bosch Process



2.2 $\Delta H^0 = -91.8 \text{ kJ mol}^{-1}$
 $\Delta S^0 = -198.1 \text{ J mol}^{-1} \text{ K}^{-1}$
 $\Delta G^0 = \Delta H^0 - T \cdot \Delta S^0 = -32.7 \text{ kJ mol}^{-1}$

The reaction is exothermic and exergonic under standard conditions.

2.3 Ammonia will form instantaneously, but the activation energy for the reaction will be so high that the two gases won't react. The reaction rate will be very low.

2.4 The enthalpy of formation is described by $\Delta_f H(T) = \Delta_f H^0 + \int_{T^0}^T C_P(T) dT$.

For N_2 : $\Delta_f H(800 \text{ K}) = 15.1 \text{ kJ mol}^{-1}$, $\Delta_f H(1300 \text{ K}) = 31.5 \text{ kJ mol}^{-1}$.

For H_2 : $\Delta_f H(800 \text{ K}) = 14.7 \text{ kJ mol}^{-1}$, $\Delta_f H(1300 \text{ K}) = 29.9 \text{ kJ mol}^{-1}$.

For NH_3 : $\Delta_f H(800 \text{ K}) = -24.1 \text{ kJ mol}^{-1}$, $\Delta_f H(1300 \text{ K}) = 4.4 \text{ kJ mol}^{-1}$.

This leads to a reaction enthalpy of:

$$\Delta H(800\text{K}) = -107.4 \text{ kJ mol}^{-1}, \quad \Delta H(1300\text{K}) = -112.4 \text{ kJ mol}^{-1}.$$

Entropy can be calculated directly with this equation..

For N_2 : $S(800\text{K}) = 220.6 \text{ J (mol K)}^{-1}$, $S(1300 \text{ K}) = 236.9 \text{ J (mol K)}^{-1}$.

For H_2 : $S(800\text{K}) = 159.2 \text{ J (mol K)}^{-1}$, $S(1300 \text{ K}) = 174.5 \text{ J (mol K)}^{-1}$.

For NH_3 : $S(800\text{K}) = 236.4 \text{ J (mol K)}^{-1}$, $S(1300 \text{ K}) = 266.2 \text{ J (mol K)}^{-1}$.

This leads to a reaction entropy of:

$$S(800\text{K}) = -225.4 \text{ J (mol K)}^{-1}, \quad S(1300\text{K}) = -228.0 \text{ J (mol K)}^{-1}.$$

Gibbs energy is:

$$\Delta G(800\text{K}) = 72.9 \text{ kJ mol}^{-1}, \quad \Delta G(1300\text{K}) = 184.0 \text{ kJ mol}^{-1}.$$

The reaction is still exothermic but now endergonic.

2.5 The equilibrium constant can be calculated from Gibbs energy according to $K_x(T) = \exp(-\Delta G(RT)^{-1})$.

This leads to the following equilibrium constants:

$$K_x(298.15\text{K}) = 5.36 \cdot 10^5,$$

$$K_x(800\text{K}) = 1.74 \cdot 10^{-5},$$

$$K_x(1300\text{K}) = 4.04 \cdot 10^{-8}.$$

Using $K_x = \frac{x_{\text{NH}_3}^2}{x_{\text{H}_2}^3 \cdot x_{\text{N}_2}}$, $x_{\text{H}_2} = 3x_{\text{N}_2}$, and $1 = x_{\text{NH}_3} + x_{\text{N}_2} + x_{\text{H}_2}$

we obtain $K_x = \frac{(1 - 4x_{\text{N}_2})^2}{27x_{\text{N}_2}^4}$.

This equation can be converted into $x_{\text{N}_2}^2 + \frac{4}{\sqrt{27K_x}} x_{\text{N}_2} - \frac{1}{\sqrt{27K_x}} = 0$

which has only one solution, since K_x and x_{N_2} are always positive:

$$x_{\text{N}_2} = -\frac{2}{\sqrt{27K_x}} + \sqrt{\frac{4}{27K_x} + \frac{1}{\sqrt{27K_x}}}.$$

We obtain the following table:

$T \cdot K^{-1}$	X_{N_2}	X_{H_2}	X_{NH_3}
298.15	0.01570	0.04710	0.03720
800	0.24966	0.74898	0.00136
1300	0.24998	0.74994	0.00008

- 2.6 The catalyst reduces the activation energy of the process and increases the reaction rate. The thermodynamic equilibrium is unchanged.
- 2.7 Higher pressures will result in a higher mol fraction of NH_3 , since $K_x = K_p \cdot p^2$ increases. An increase in pressure shifts the equilibrium toward the products but does not change the reaction rate.
- 2.8 The best conditions are: high pressure, temperature as low as possible and the presence of a catalyst. The temperature has to be optimized such that the turnover is fast and the yield still acceptable.

Solution Problem 3: Thermodynamics in Biochemistry

$$\begin{aligned}
 3.1 \quad \Delta G^0 &= -RT \ln K \\
 &= -RT \ln \frac{c(\text{lactate}) \cdot c(\text{NAD}^+)}{c(\text{pyruvate}) \cdot c(\text{NADH}) \cdot c(\text{H}^+)} \\
 &= -RT \ln \frac{c(\text{lactate}) \cdot c(\text{NAD}^+)}{c(\text{pyruvate}) \cdot c(\text{NADH})} - RT \ln \frac{1}{c(\text{H}^+)}
 \end{aligned}$$

$$\Delta G^0 = -RT \ln \frac{c(\text{lactate}) \cdot c(\text{NAD}^+)}{c(\text{pyruvate}) \cdot c(\text{NADH})}$$

$$\begin{aligned}
 \Delta G^0 &= \Delta G^{0'} - RT \cdot \ln(c(\text{H}^+)^{-1}) \\
 &= -25100 \text{ J mol}^{-1} - 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \cdot 298.15 \text{ K} \cdot \ln 10^7 \\
 &= -25.1 \text{ kJ mol}^{-1} - 40.0 \text{ kJ mol}^{-1} \\
 &= -65.1 \text{ kJ mol}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 3.2 \quad \Delta G^{0'} &= -RT \ln K' & K' &= e^{-\Delta G^0 / (RT)} \\
 K' &= e^{25100 / (8.314 \cdot 298.15)} & K' &= 2.5 \cdot 10^4
 \end{aligned}$$

$$\begin{aligned}
 3.3 \quad \Delta G' &= \Delta G^{0'} + RT \ln \frac{c(\text{prod.})}{c(\text{react.})} \\
 &= \Delta G^{0'} + RT \ln \frac{c(\text{lactate}) \cdot c(\text{NAD}^+)}{c(\text{pyruvate}) \cdot c(\text{NADH})} \\
 &= -25100 \text{ J mol}^{-1} + 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \cdot 298.15 \text{ K} \cdot \ln(3700 \cdot 540 / (380 \cdot 50)) \\
 &= -25.1 \text{ kJ mol}^{-1} + 11.5 \text{ kJ mol}^{-1} \\
 &= -13.6 \text{ kJ mol}^{-1}
 \end{aligned}$$

Solution problem 4: Heat Conductivity

4.1 The heat flows are:

$$P_W = 150 \text{ m}^2 \cdot (0.24 \text{ m})^{-1} \cdot 0.81 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1} \cdot (25^\circ\text{C}-10^\circ\text{C}) = 7.59 \text{ kW and}$$

$$P_W = 150 \text{ m}^2 \cdot (0.36 \text{ m})^{-1} \cdot 0.81 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1} \cdot (25^\circ\text{C}-10^\circ\text{C}) = 5.06 \text{ kW}$$

4.2 $P_W = 150 \text{ m}^2 \cdot (0.1 \text{ m})^{-1} \cdot 0.040 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1} \cdot (25^\circ\text{C}-10^\circ\text{C}) = 0.90 \text{ kW}$

Although the wall is much thinner, the energy loss is much lower due to the much lower heat conductivity.

4.3 $k = \lambda \cdot d^{-1} \rightarrow d = \lambda \cdot k^{-1} = 0.81 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1} \cdot (0.5 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1})^{-1} \quad d = 1.62 \text{ m}$

4.4 $\Lambda^{-1} = k^{-1} = (0.50 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1})^{-1} = d_1 \cdot (\lambda_1)^{-1} + d_2 \cdot (\lambda_2)^{-1} + d_3 \cdot (\lambda_3)^{-1} + d_4 \cdot (\lambda_4)^{-1} =$
 $0.15 \text{ m} \cdot (0.81 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1})^{-1} + 0.10 \text{ m} \cdot (1.1 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1})^{-1} + d_3 \cdot (0.040 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1})^{-1} + 0.05 \text{ m} \cdot$
 $(0.35 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1})^{-1}$

The thickness of the insulation foam layer is $d_3 = 6.3 \text{ cm}$

The total thickness is: $15 \text{ cm} + 10 \text{ cm} + 6.3 \text{ cm} + 5 \text{ cm} = 36.3 \text{ cm}$

4.5 $k = \Lambda_1 \cdot A_1 \cdot (A_{\text{tot}})^{-1} + \Lambda_2 \cdot A_2 \cdot (A_{\text{tot}})^{-1}$
 $0.50 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1} = 0.70 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1} \cdot 4 \text{ m}^2 \cdot (15 \text{ m}^2)^{-1} + \Lambda_2 \cdot 11 \text{ m}^2 \cdot (15 \text{ m}^2)^{-1}$
 $\Lambda_2 = 0.427 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$.

The calculation is similar to that of 4.4:

The thickness of the insulation foam layer is $d_3 = 7.7 \text{ cm}$

The total thickness is: $5 \text{ cm} + 10 \text{ cm} + 7.7 \text{ cm} + 5 \text{ cm} = 37.7 \text{ cm}$

due to the much higher heat conductivity of the window.

The thickness of the foam layer has to be increased by 22%.

Solution problem 5: Supercritical CO₂

5.1 $dW = -n \cdot R \cdot T \cdot dV \cdot V^{-1}$ or $W = -n \cdot R \cdot T \cdot \ln(p_1/p_2)$

$$n = p \cdot V \cdot (R \cdot T)^{-1} = (50 \cdot 10^5 \text{ Pa} \cdot 50 \cdot 10^{-6} \text{ m}^3) \cdot (8.314 \text{ JK}^{-1} \text{ mol}^{-1} \cdot 298 \text{ K})^{-1} = 0.10 \text{ mol}$$

$$W = -0.10 \text{ mol} \cdot 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \cdot 298 \text{ K} \cdot \ln(1/50) = 969 \text{ J}$$

5.2 The calculation can be most easily carried out with the molar volume $V_m = M \cdot \rho^{-1}$. The equation $[p + a \cdot (n \cdot V^{-1})^2] \cdot (V - n \cdot b) = n \cdot R \cdot T$ can be simplified to

$$[p + a \cdot V_m^{-2}] \cdot (V_m - b) = R \cdot T$$

Example of the calculation (density $\rho = 440 \text{ g dm}^{-3}$ or $V_m = 0.10 \text{ dm}^3 \text{ mol}^{-1}$; $T = 305 \text{ K}$)

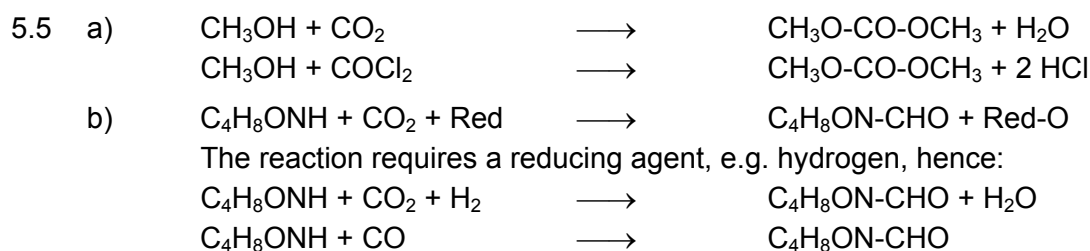
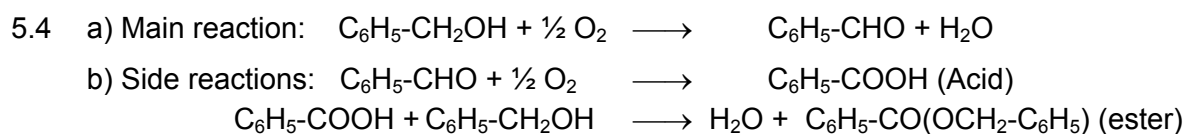
$$[p + (3.59 \cdot 10^5 \text{ Pa} \cdot 10^{-6} \text{ m}^6 \text{ mol}^{-2}) \cdot (0.1^2 \cdot 10^{-6} \text{ m}^6 \text{ mol}^{-2})^{-1}] \cdot$$

$$(0.1 \cdot 10^{-3} \text{ m}^3 \text{ mol}^{-1} - 0.0427 \cdot 10^{-3} \text{ m}^3 \text{ mol}^{-1}) = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \cdot 305 \text{ K}$$

$$p = 83.5 \cdot 10^5 \text{ Pa}$$

$\rho \cdot (\text{g}\cdot\text{dm}^{-3})^{-1}$	$V_m \cdot (\text{dm}^3\cdot\text{mol}^{-1})^{-1}$	$T \cdot \text{K}^{-1}$	$p \cdot \text{Pa}^{-1}$
220	0.200	305	$71.5 \cdot 10^5$
330	0.133	305	$77.9 \cdot 10^5$
440	0.100	305	$83.5 \cdot 10^5$
220	0.200	350	$95.2 \cdot 10^5$
330	0.133	350	$119.3 \cdot 10^5$
440	0.100	350	$148.8 \cdot 10^5$

5.3 The results in the table above show that a 10 bar change in pressure near the critical temperature results in nearly double the density. Far above the critical temperature, however, such a change requires higher pressures. Hence, it is useful to work near the critical temperature/pressure.

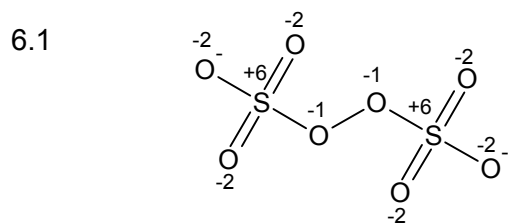


5.6 The advantage of using carbon dioxide is that it is not poisonous in contrast to carbon monoxide and phosgene. CO_2 makes the process safer. Moreover, using CO_2 both as reactant and as solvent is advantageous, since no additional solvent is necessary.

Another reason may be the reduction of the CO_2 -emission, but this will not be significant.

One of the disadvantages is that CO_2 is much less reactive than CO or COCl_2 – therefore a search for suitable catalysts is inevitable (catalysts have been found only for a few reactions, such as the formylation of amines).

Solution problem 6: Chemical Kinetics of the Peroxodisulfate Ion



6.2 $r = k \cdot c(\text{S}_2\text{O}_8^{2-}) \cdot c(\text{I}^-)$

6.3 reaction order: 2

partial reaction order of $\text{S}_2\text{O}_8^{2-}$: 1

partial reaction order of I^- : 1

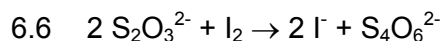
6.4 $k = \frac{r}{c(\text{S}_2\text{O}_8^{2-}) \cdot c(\text{I}^-)} = \frac{1.1 \cdot 10^{-8} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}}{0.1 \cdot 10^{-3} \cdot 1 \cdot 10^{-2} \text{ mol}^2 \cdot \text{L}^{-2}} = 0.011 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$

6.5 Using the Arrhenius equation we may write

$$k_1 = A \cdot e^{-\frac{E_a}{R \cdot T_1}}, k_2 = A \cdot e^{-\frac{E_a}{R \cdot T_2}} \quad \Rightarrow \quad \frac{k_1}{k_2} = e^{\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)}$$

because $k_1/k_2 = 1/10$, it follows that

$$\ln \frac{1}{10} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \Leftrightarrow \frac{1}{T_2} = \frac{R}{E_a} \cdot \ln \frac{1}{10} + \frac{1}{T_1} \quad \Rightarrow T_2 = 345 \text{ K} \approx 72^\circ\text{C}$$



6.7 It has to be noticed that the concentration of the iodide ions does not vary any longer, because iodine formed reacts quickly with thiosulfate ions (which are available in excess according to the precondition) forming iodide ions again.

Therefore the reaction is of pseudo-1st-order and the rate equation is given by $r = k' \cdot c(\text{S}_2\text{O}_8^{2-})$

(It is important to note that the rate constant k' is different from k of the parts 6.2 - 6.5 of this problem, because it includes the pseudo-constant concentration of the iodide ions).

Solution problem 7: Catalytic Hydrogenation of Ethylene

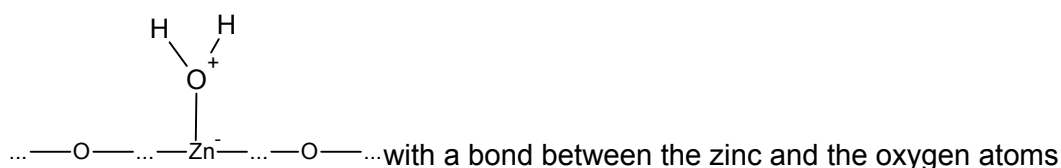
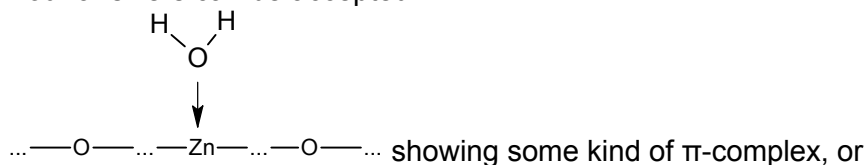
7.1

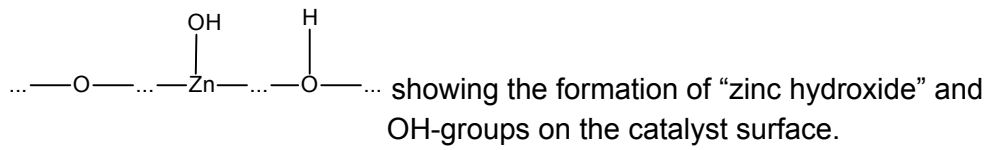
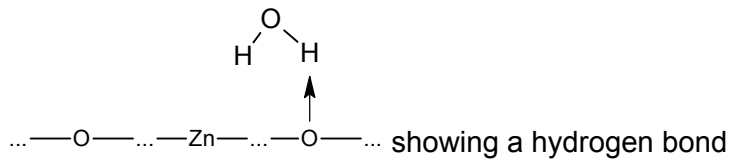
No.		No.	
1	$\text{H} \text{---} \text{H}$...—O—...—Zn—...—O—...	5	$\text{H}_2\text{C}=\text{CH}_2$ H H ...—O—...—Zn—...—O—...
3	H H ...—O—...—Zn—...—O—...	7	$\text{H}_3\text{C} \text{---} \text{CH}_3$...—O—...—Zn—...—O—...
4	$\text{H}_2\text{C}=\text{CH}_2$ H H ...—O—...—Zn—...—O—...	2	H H ...—O—...—Zn—...—O—...
6	CH ₃ CH ₂ H ...—O—...—Zn—...—O—...		

7.2 The hydrogenation of the adsorbed intermediate is the slowest step of the reaction. This is the reason why the concentration, or in this case the fraction of surface sites that are occupied, has to be part of the rate equation.

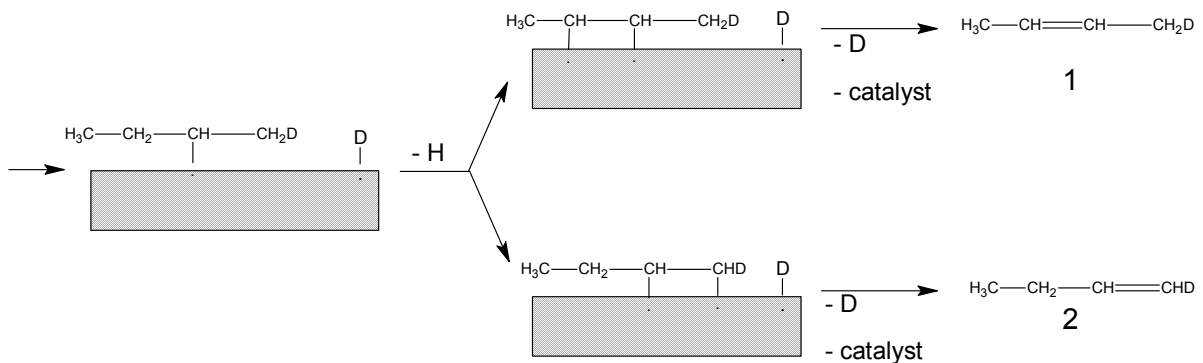
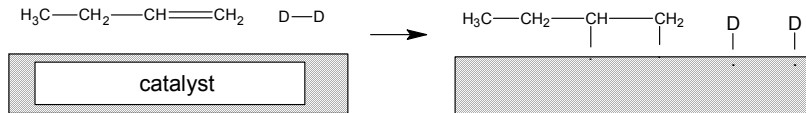
Answer (4) is correct.

7.3 Four answers can be accepted:





7.4



7.5 Knowing the derivation of the Langmuir isotherm from the law of mass action you can obtain:

$$\theta(i) = \frac{K_i \cdot p_i}{1 + \sum_j K_j \cdot p_j}$$

Solution problem 8: Kinetics of an Enzymatic Reaction

8.1 $x = 1, y = -1, z = 1$

8.2. $\frac{dc(E)}{dt} = -k_1c(S)c(E) + k_{-1}c(ES) + k_2c(ES)$

8.3 The reciprocal rate is plotted as a function of the reciprocal substrate concentration:

$$\frac{1}{r} = \frac{K_M}{k_2c_T(E)} \cdot \frac{1}{c(S)} + \frac{1}{k_2c_T(E)}$$

Intercept at $1/c(S) = 0$ yields $\frac{1}{r} = \frac{1}{k_2 c_T(E)} = 0.02 \cdot 10^6 \text{ L min mol}^{-1}$

With $c_T(E) = 10^{-9} \text{ mol L}^{-1}$ we obtain $k_2 = 50000 \text{ min}^{-1}$

Intercept at $1/r = 0$ yields $\frac{1}{c(S)} = -\frac{1}{K_M} = -0.09 \cdot 10^6 \text{ L mol}^{-1}$

$K_M = 1.1 \cdot 10^{-5} \text{ mol L}^{-1}$.

Alternatively, the slope is $\frac{K_M}{k_2 c_T(E)} = 0.22 \text{ min}$

$K_M = 1.1 \cdot 10^{-5} \text{ mol L}^{-1}$

The rate of the enzymatic reaction is given as

$$\frac{dc(P)}{dt} = k_2 c(ES) = k_2 c_T(E) \frac{c(S)}{K_M + c(S)}$$

$$c(ES) = c_T(E) \frac{c(S)}{K_M + c(S)}$$

$$c(ES) = c_T(E) \frac{0.01 K_M}{K_M + 0.01 K_M}$$

$$c(ES) = 9.9 \cdot 10^{-3} c_T(E)$$

$$c(ES) = 9.9 \cdot 10^{-12} \text{ mol L}^{-1}$$

8.4 $K = \frac{c(I)c(E)}{c(EI)} = \frac{c(I) \cdot 0.5c_T(E)}{0.5c_T(E)} = c(I) = 9.5 \cdot 10^{-4} \text{ mol L}^{-1}$

The total inhibitor concentration is

$$c_T(I) = c(I) + c(EI) = K + 0.5 \cdot c_T(E) = 1.35 \cdot 10^{-3} \text{ mol L}^{-1}$$

- 8.5 true (the inhibitor reduces the free enzyme concentration and thus the rate of ES formation. A lower ES concentration results and leads to a smaller reaction rate)
 false (the maximum rate is reached for $c(S) = \infty$ where the inhibitor concentration can be ignored)
 false (the inhibitor reduces the free enzyme concentration and thus promotes the dissociation of the complex ES into E and S (Le Chatelier's principle))
 false (the activation energy depends on the rate constants that are independent of concentrations)

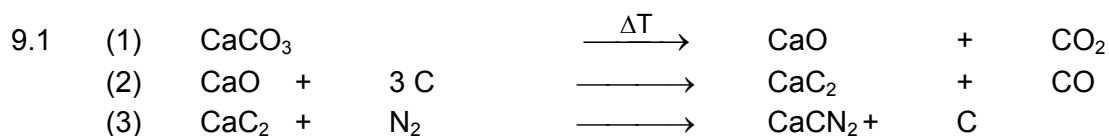
8.6 The enzyme is only a catalyst. The net reaction is $S \rightleftharpoons P$

true (because $K = c^{eq}(P) / c^{eq}(S)$)

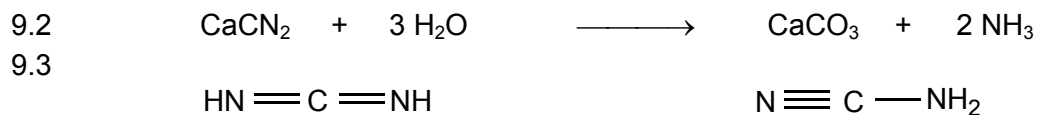
false (because K does not depend on the enzyme concentration)

true (because K is the ratio of the rate constants for the forward and the reverse reaction)

Solution problem 9: CaCN_2 – An Old but still Important Fertilizer



This process that is technically important is called the Frank-Caro process.

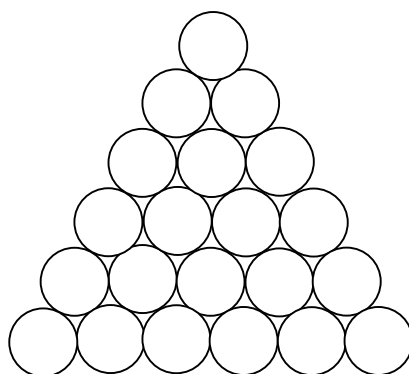


The first compound is the acid of the carbodiimide ion, the second is that of cyanamide. The equilibrium favours the more symmetric structure.

(Inorg.Chem. 2002, 41, 4259 - 4265)

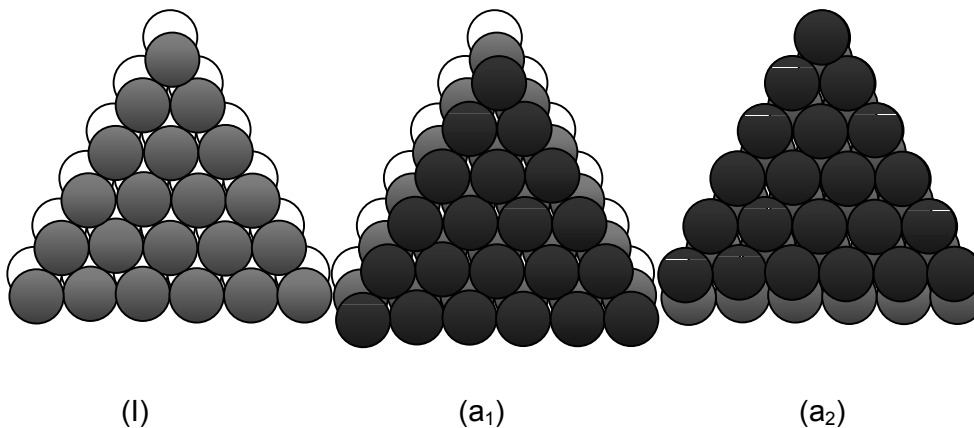
Solution problem 10 : Closed-Packed Structures

10.1



In the two-dimensional model each indistinguishable atom is surrounded by six other atoms.

10.2

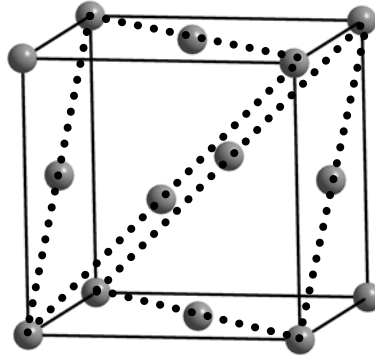


A transformation into a three-dimensional model can be achieved by stacking the 2D closed-packed layers (I). Each atom has six neighbours in the plane surrounding it, and three further atoms located in the holes above the atom and three atoms located in the holes below the atom.

- a) Looking at the second layer, there are two possibilities of putting a third layer on top. Either the atoms are put into the holes such that there is no atom directly beneath them in the first layer (a₁), or into the same positions they occupy in the first layer (a₂). These possibilities create the two different closed-packed structures, ABCABC (cubic closed-packed) and ABAB (hexagonal closed packed).

- b) In principle, an infinite number of stacking patterns can be generated by the combination of these two basic stacking possibilities.

10.3



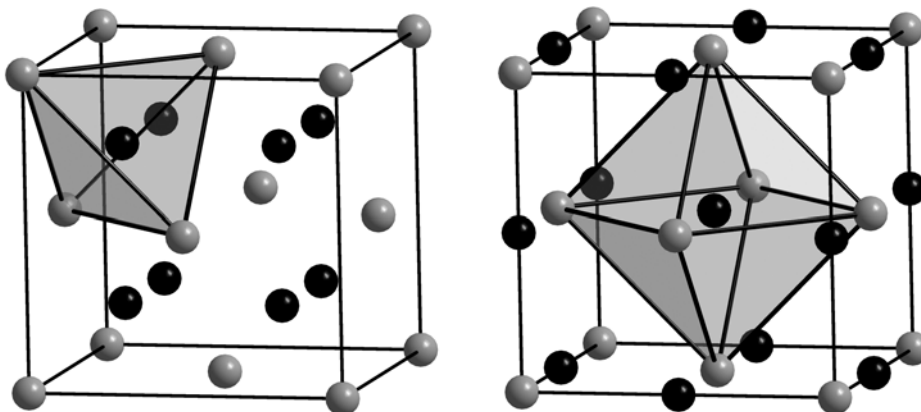
- 10.4 In this illustration, the atoms touch on the face diagonals. The length of the edges of the cube is $2r \cdot \sqrt{2}$. There are 4 complete atoms in the cube (8 corners with one eighth of an atom in each and 6 sides with one half of an atom in the middle of each). So the packing efficiency is:

$$\frac{4 \cdot \frac{4}{3} \pi r^3}{(2r\sqrt{2})^3} = \frac{16}{3} \frac{\pi r^3}{16r^3\sqrt{2}} = \frac{\pi}{3\sqrt{2}} = 0.74 \text{ or } 74\%$$

A cubic primitive packing has a packing efficiency of:

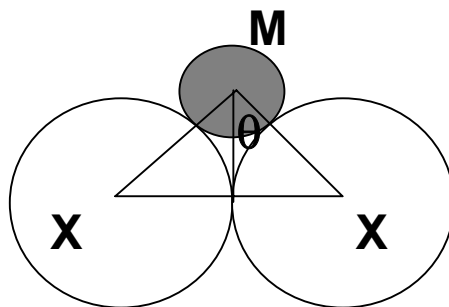
$$\frac{1 \cdot \frac{4}{3} \pi r^3}{(2r)^3} = \frac{4}{8} \pi = 0.52 \text{ or } 52\%$$

10.5



The elemental cube of a face centered cubic structure contains 4 packing atoms (one at the corner and three on the faces of the cube), eight tetrahedral holes (one in each octant of the cube) and 4 octahedral holes (one in the centre of the cube, 12 additional holes in the middle of the edges of the cube, each shared of 4 cubes).

10.6



A line perpendicular to the edge divides the tetrahedral angle into two halves. The length of the edge is $2 r_X$. The distance from a tetrahedral vertex to the center is $r_M + r_X$. The angle is $109,5^\circ/2$.

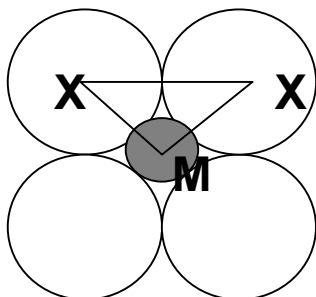
$$\sin \theta = r_X / (r_M + r_X)$$

$$0.816 r_M = 0.184 r_X$$

$$\sin (109,5^\circ/2) \cdot (r_M + r_X) = r_X$$

$$r_M/r_X = 0.225$$

10.7



$$(2r_X)^2 = (r_M + r_X)^2 + (r_M + r_X)^2$$

$$4r_X^2 = 2 (r_M + r_X)^2$$

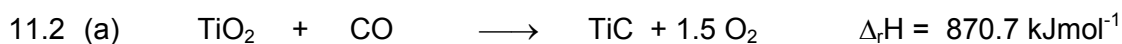
$$\sqrt{2} r_X = r_M + r_X$$

$$r_M/r_X = (\sqrt{2} - 1) = 0.414$$

$$r_M/r_X = 0.414$$

Solution problem 11: Titanium Carbide – A High-Tech Solid

11.1 $r(\text{Ti}^{4+})/r(\text{C}^{4-}) = 0.527 \rightarrow \text{NaCl-type}$



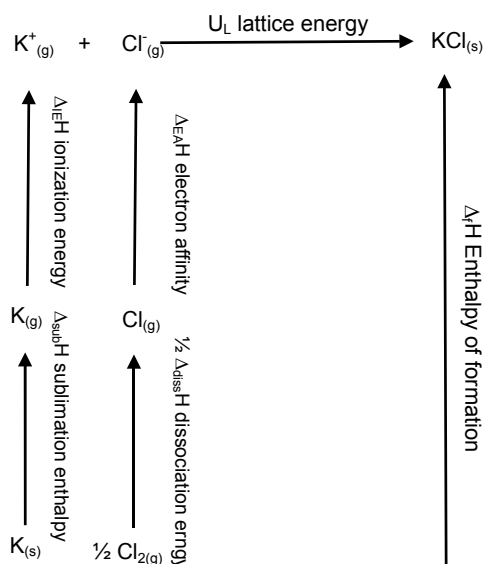
(a) + 3·(b) :



$\Delta_r H = (870.7 + 3 \cdot (-110.5)) \text{ kJmol}^{-1}$

$\Delta_r H = 539.2 \text{ kJmol}^{-1}$

11.3.



$$-U_L = \Delta_{\text{sub}}H + \Delta_{\text{IE}}H + 0.5 \cdot \Delta_{\text{diss}}H + \Delta_{\text{EA}}H - \Delta_fH$$

$$U_L = -(89 + 425 + 122 - 355 + 438 \text{ kJ mol}^{-1})$$

$$U_L = -719 \text{ kJ mol}^{-1}$$

(If the lattice energy is defined in the opposite way the result will be + 719 kJmol⁻¹)

Solution problem 12: Metal Nanoclusters

12.1 The potential of a half-cell is described by the Nernst equation:

$$E = E^0 + \frac{RT}{nF} \cdot \ln \frac{c(\text{ox})}{c(\text{red})}$$

The total voltage is: $U = E(\text{cathode}) - E(\text{anode})$

$$E = E^0 + RTF^{-1} \ln(c(\text{Ag}^+) \text{ mol}^{-1}\text{L})$$

$$U_1 = E_2 - E_1 \text{ and } U_1 = \frac{RT}{F} \cdot \ln \frac{c_2(\text{Ag}^+)}{c_1(\text{Ag}^+)}$$

and with $U_1 = 0.170 \text{ V}$ $c_2(\text{Ag}^+) = 0.01 \text{ mol L}^{-1}$ $c_1(\text{Ag}^+) = x \text{ mol L}^{-1}$

$$0.170 \text{ V} = \frac{8.314 \cdot 298.15}{96485} \text{ V} \cdot \ln \frac{c_2(\text{Ag}^+)}{c_1(\text{Ag}^+)}$$

$$c_1(\text{Ag}^+) = 1.337 \cdot 10^{-5} \text{ mol L}^{-1}$$

In the saturated solution $c(\text{Ag}^+) = c(\text{Cl}^-) = 1.337 \cdot 10^{-5} \text{ mol L}^{-1}$ and thus

$$K_{\text{sp}} = (1.337 \cdot 10^{-5} \text{ mol L}^{-1})^2 \quad K_{\text{sp}} = 1.788 \cdot 10^{-10} \text{ mol}^2\text{L}^{-2}$$

12.2 For the right cell of (II): $E(\text{AgCl}) = 0.8 \text{ V} + RTF^{-1} \ln(1.337 \cdot 10^{-5})$

$$E(\text{AgCl}) = 0.512 \text{ V}$$

thus $U = E(\text{AgCl}) - E(\text{Ag}_n, \text{Ag}^+)$

and $E(\text{Ag}_n/\text{Ag}^+) = E^0(\text{Ag}_n/\text{Ag}^+) + RTF^{-1} \ln(0.01)$

Ag_{10} : $E(\text{Ag}_{10}/\text{Ag}^+) = 0.512 \text{ V} - 0.430 \text{ V} = 0.082 \text{ V}$

$$E^0(\text{Ag}_{10}/\text{Ag}^+) = 0.082 \text{ V} - RTF^{-1} \ln(0.01) \quad E^0(\text{Ag}_{10}/\text{Ag}^+) = 0.200 \text{ V}$$

Ag_5 : $E(\text{Ag}_5/\text{Ag}^+) = 0.512 \text{ V} - 1.030 \text{ V} = -0.518 \text{ V}$

$$E^0(\text{Ag}_5/\text{Ag}^+) = -0.518 \text{ V} - RTF^{-1} \ln(0.01) \quad E^0(\text{Ag}_5/\text{Ag}^+) = -0.400 \text{ V}$$

12.3 The standard potential increases with increasing particle size until it reaches the bulk value at a certain particle size.

The potential is lower for smaller particles, because they have a larger surface and the process of crystallization is energetically less favourable for the surface atoms. Thus, the free energy of formation of metallic silver is larger (less negative) for smaller particles, i.e. the standard potential is lower. The effect decreases with increasing particle size due to the decreasing relative amount of surface atoms.

Additional remark: However, the potential does not continuously increase with increasing size. The electrochemical potentials of some small clusters of a certain size are much higher. This is due to complete shells of these clusters (clusters consist of a "magic number" of atoms) which make them more stable.

(Instead of the crystallization energy you can also argue with the sublimation energies of silver atoms.)

12.4 a) For a solution with a pH of 13:

$$E(\text{H}_2/2\text{H}^+) = \text{RTF}^{-1}\ln(10^{-7}) \quad E(\text{H}_2/2\text{H}^+) = -0.769 \text{ V}$$

As an estimate, this potential can be compared with the standard potentials of the silver clusters calculated in 12.2. Both are higher than the standard potential of hydrogen. Thus, the silver clusters behave as noble metals and are not oxidized in this solution. No reaction takes place.

Quantitatively, a small amount of silver is oxidized into Ag^+ ions until equilibrium is reached and $E(\text{Ag}_n/\text{Ag}^+) = E(\text{H}_2/2\text{H}^+)$.

$$E^0(\text{Ag}_n/\text{Ag}^+) + \text{RTF}^{-1}\ln(c(\text{Ag}^+) \text{ mol}^{-1}\text{L}) = -0.769 \text{ V}$$

$$\text{for Ag}_{10}: c(\text{Ag}^+) = 4.17 \cdot 10^{-17} \text{ mol L}^{-1} \quad \text{and for Ag}_5: c(\text{Ag}^+) = 5.78 \cdot 10^{-7} \text{ mol L}^{-1}$$

b) For a solution with a pH of 5:

$$E(\text{H}_2/2\text{H}^+) = \text{RTF}^{-1}\ln(10^{-2}) \quad E(\text{H}_2/2\text{H}^+) = -0.269 \text{ V}$$

As an estimate, the standard potential of the Ag_{10} clusters is higher than the standard potential of the hydrogen. No reaction takes place. The standard potential of the Ag_5 clusters is lower than the standard potential of hydrogen. Thus, hydronium ions will be reduced to hydrogen while Ag_5 clusters (metallic silver) are oxidized into silver ions: The Ag-clusters dissolve.

Quantitatively, equilibrium is reached for Ag_{10} at: $c(\text{Ag}^+) = 4.16 \cdot 10^{-9} \text{ mol L}^{-1}$

and for Ag_5 at: $c(\text{Ag}^+) = 57.29 \text{ mol L}^{-1}$ (which will probably not be reached in a diluted solution and all nanoclusters dissolve)

(After some time, silver ions that are present in the solution can also be reduced to metallic bulk silver. Under this condition, this reduction will preferably take place, because the electrochemical potential is even higher than that of the hydronium-ion reduction.)

c) Potentials of all possible reactions are considered:

$$1. \quad E(\text{Cu}/\text{Cu}^{2+}) = 0.345 \text{ V} + 0.5 \cdot \text{RTF}^{-1}\ln(0.001) = 0.256 \text{ V}$$

$$2. \quad E(\text{Ag}/\text{Ag}^+) = 0.800 \text{ V} + \text{RTF}^{-1}\ln(10^{-10}) = 0.208 \text{ V}$$

$$3. \quad E(\text{Ag}_{10}/\text{Ag}^+) = 0.200 \text{ V} + \text{RTF}^{-1}\ln(10^{-10}) = -0.392 \text{ V}$$

$$4. \quad E(\text{Ag}_5/\text{Ag}^+) = -0.400 \text{ V} + \text{RTF}^{-1}\ln(10^{-10}) = -0.992 \text{ V}$$

$$5. \quad E(\text{H}_2/2\text{H}^+) = \text{RTF}^{-1}\ln(10^{-7}) = -0.414 \text{ V}$$

The reduction with the highest potential and the oxidation with the lowest potential will preferably take place: Copper(II) ions will be reduced into metallic copper while Ag_5 clusters dissolve and form silver(I) ions.

After some time, the silver concentration of the solution increases, Ag_5 clusters are used up and the concentration of copper ions decreases. Since the latter is comparably high, it is expected to have minor influence. The next possible steps of the reaction are the following:

- (i) After the Ag_5 clusters are used up, Ag_{10} clusters will start to be oxidized. (Note that if a hydrogen electrode was present, H_2 would be oxidized. In this system, however, there are protons instead of H_2).
- (ii) After the increase of the silver ion concentration, the potential of the silver ion reduction (into metallic bulk silver) increases, so that it might exceed the potential of the copper reduction. Afterwards, the silver ions will be reduced to metallic silver (after further dissolution of silver nanoclusters).

Solution problem 13: Absorption of Light by Molecules

13.1 $A = \epsilon cd = 1.5 \cdot 10^5 \text{ mol}^{-1} \text{ L cm}^{-1} \cdot 4 \cdot 10^{-6} \text{ mol L}^{-1} \cdot 10^{-4} \text{ cm} = 6 \cdot 10^{-5}$

Since $A = \log(P_0/P)$, the ratio P/P_0 is 0.999862. This is the percentage of photons exiting the sample, so that the percentage of photons absorbed by the solution is:

$$\frac{P_0 - P}{P_0} = 1 - \frac{P}{P_0} = 1.38 \cdot 10^{-4} \text{ or } 0.0138\%.$$

13.2 According to our previous result, 0.0138% of the 10 nW laser light entering the sample solution are absorbed:

$$P_{\text{abs}} = 1.38 \cdot 10^{-4} \cdot 10 \text{ nW} = 1.38 \cdot 10^{-3} \text{ nW} = 1.38 \cdot 10^{-12} \text{ J s}^{-1}$$

The energy of one photon is:

$$E = hc/\lambda = 6.626 \cdot 10^{-34} \text{ J s} \cdot 3.00 \cdot 10^8 \text{ m s}^{-1} / (514.5 \cdot 10^{-9} \text{ m}) = 3.86 \cdot 10^{-19} \text{ J}$$

The number of photons absorbed by the solution per second is:

$$N_{\text{abs}} = 1.38 \cdot 10^{-12} \text{ J s}^{-1} / 3.86 \cdot 10^{-19} \text{ J} = 3.58 \cdot 10^6 \text{ s}^{-1}.$$

13.3 Let's imagine that the laser illuminates an area of 1 cm^2 of the dye solution. The light beam passes through a volume of $V = 1 \text{ cm}^2 \cdot 1 \mu\text{m} = 10^{-7} \text{ L}$. The number of illuminated molecules is:

$$N = cVN_A = 4 \cdot 10^{-6} \text{ mol L}^{-1} \cdot 10^{-7} \text{ L} \cdot 6.022 \cdot 10^{23} \text{ mol}^{-1} = 2.409 \cdot 10^{11}$$

Each molecule would therefore occupy an area of

$$S_{\text{mol}} = 1 \text{ cm}^2 / 2.409 \cdot 10^{11} = 4.15 \cdot 10^{-12} \text{ cm}^2 \text{ or } 415 \text{ nm}^2, \text{ if it was projected onto a plane.}$$

13.4 The molecular absorption cross section σ is the area of one molecule that captures all incoming photons. Under the experimental conditions, only 0.0138% of the light interacting with one molecule is absorbed, so that σ is:

$$\sigma = 1.38 \cdot 10^{-4} \cdot 415 \text{ nm}^2 = 0.057 \text{ nm}^2 = 5.7 \text{ \AA}^2$$

13.5 The energy of one 680 nm photon is:

$$E = hc/\lambda = 6.626 \cdot 10^{-34} \text{ J s} \cdot 3.00 \cdot 10^8 \text{ m s}^{-1} / (680 \cdot 10^{-9} \text{ m}) = 2.92 \cdot 10^{-19} \text{ J}$$

Photosynthesis requires 59 kJ per mol of ATP, which corresponds to

$$E_{\text{ATP}} = 59 \cdot 10^3 \text{ J mol}^{-1} / 6.022 \cdot 10^{23} \text{ mol}^{-1} = 9.80 \cdot 10^{-20} \text{ J per ATP molecule.}$$

The energy efficiency of photosynthesis is:

$$\eta = 9.80 \cdot 10^{-20} \text{ J} / 2.92 \cdot 10^{-19} \text{ J} = 0.34 \text{ or } 34\%.$$

Solution problem 14: Observing Single Molecules

14.1. Molecular fluorescence in the visible region is due to delocalized electrons in extended π -systems, so the correct answer is:

(4) The C-N chain connecting the two benzene rings

14.2 A circle with a diameter of 4 mm covers a surface area of

$$S = \pi r^2 \text{ with } r = 2 \cdot 10^{-3} \text{ m, so } S = 1.26 \cdot 10^{-5} \text{ m}^2$$

The number of molecules in this area is:

$$10 / (10^{-6} \text{ m})^2 \cdot 1.26 \cdot 10^{-5} \text{ m}^2 = 126 \cdot 10^6 \text{ molecules}$$

They are transferred onto the surface by the evaporation of 10 μL of solution, so the concentration has to be

$$126 \cdot 10^6 / (10 \cdot 10^{-6} \text{ L}) = 1.26 \cdot 10^{13} \text{ molecules L}^{-1}$$

which corresponds to a molar concentration of

$$c = 1.26 \cdot 10^{13} \text{ L}^{-1} / (6.022 \cdot 10^{23} \text{ mol}^{-1}) = 2.1 \cdot 10^{-11} \text{ mol L}^{-1}$$

14.3 When $E = hc/\lambda$, the energy per photon is:

$$E = hc/\lambda = 6.626 \cdot 10^{-34} \text{ J s} \cdot 3.00 \cdot 10^8 \text{ m s}^{-1} / (543.5 \cdot 10^{-9} \text{ m}) \\ = 3.66 \cdot 10^{-19} \text{ J}$$

$3 \cdot 10^{10}$ photons per second amount to an excitation power of

$$P = 3.65 \cdot 10^{-19} \text{ J} \cdot 3 \cdot 10^{10} \text{ s}^{-1} = 1.1 \cdot 10^{-8} \text{ J s}^{-1} = 11 \text{ nW}$$

14.4 On average, there are 10 molecules per μm^2 , so that one molecule occupies statistically an area of $S_{\text{mol}} = (10^{-6} \text{ m})^2 / 10 = 10^{-13} \text{ m}^2$.

The total illuminated area of $\pi \cdot (50 \cdot 10^{-9} \text{ m})^2 = 7.85 \cdot 10^{-15} \text{ m}^2$ receives $3 \cdot 10^{10}$ photons per second, and the area occupied by a single molecule receives

$$3 \cdot 10^{10} \text{ s}^{-1} \cdot 10^{-13} \text{ m}^2 / (7.85 \cdot 10^{-15} \text{ m}^2) = 3.82 \cdot 10^{11} \text{ photons per second.}$$

Only $2.3 \cdot 10^5$ photons are absorbed every second, so the area which is capturing photons is:

$$\sigma = 10^{-13} \text{ m}^2 \cdot 2.3 \cdot 10^5 \text{ s}^{-1} / (3.82 \cdot 10^{11} \text{ s}^{-1}) = 6 \cdot 10^{-20} \text{ m}^2 \text{ or } 6 \text{ \AA}^2$$

$$(\text{or } \sigma = (7.85 \cdot 10^{-15} \text{ m}^2 / 3 \cdot 10^{10} \text{ s}^{-1}) \cdot 2.3 \cdot 10^5 \text{ s}^{-1} = 6 \cdot 10^{-20} \text{ m}^2)$$

14.5 A dilC_{12} molecule that absorbs $2.3 \cdot 10^5$ photons per second emits

$N_{\text{fluo}} = 0.7 \cdot 2.3 \cdot 10^5 \text{ s}^{-1} = 161 \cdot 10^3$ fluorescence photons per second. Due to the detection efficiency, this results in

$$N_{\text{det}} = 161 \cdot 10^3 \text{ s}^{-1} \cdot 0.2 \cdot 0.55 = 17\,710 \text{ detected photons per second.}$$

In a time interval of 10 ms, the number of detected photons is:

$$17\,710 \text{ s}^{-1} \cdot 10 \cdot 10^{-3} \text{ s} = 177 \text{ photons.}$$

14.6 Each point in the illuminated sample area is hit by the same number of photons per second (uniform illumination). A molecule that is located in the spot's center is emitting as many fluorescence photons as if it was sitting anywhere else in the illuminated spot. As the illuminated area is raster-scanned across the sample surface, the molecule will be visible as long as it is inside the illuminated area. This is the reason why the fluorescence spot of one molecule will have a size equal to the illuminated area, i.e. 100 nm in diameter (14.3).

Solution probl. 15: Infrared Spectroscopy of Tetrahedral Molecules

$$15.1 \quad 2\pi\nu = \sqrt{\frac{k}{\mu}} \rightarrow$$

$$k = 4\pi^2\nu^2\mu$$

$$\nu = c \cdot \tilde{\nu}$$

from the diagram:

$$\tilde{\nu}(\text{CF}_4) = 1280 \text{ cm}^{-1}$$

$$\tilde{\nu}(\text{SiF}_4) = 1010 \text{ cm}^{-1}$$

hence

$$\nu(\text{CF}_4) = 38.4 \cdot 10^{12} \text{ s}^{-1}$$

$$\nu(\text{SiF}_4) = 30.3 \cdot 10^{12} \text{ s}^{-1}$$

$$\mu = \frac{3m_X \cdot m_Y}{3m_X + 4m_Y}$$

$$\mu(\text{CF}_4) = 6.11 \text{ g} \cdot \text{mol}^{-1} \cdot \text{N}_A^{-1}$$

$$\mu(\text{SiF}_4) = 9.99 \text{ g} \cdot \text{mol}^{-1} \cdot \text{N}_A^{-1}$$

$$\mu(\text{CF}_4) = 1.01 \cdot 10^{-23} \text{ g}$$

$$\mu(\text{SiF}_4) = 1.66 \cdot 10^{-23} \text{ g}$$

$$\text{hence } k(\text{CF}_4) = 4\pi^2 \cdot (38.4 \cdot 10^{12} \text{ s}^{-1})^2 \cdot 1.01 \cdot 10^{-23} \text{ g} \quad k(\text{CF}_4) = 588 \text{ Nm}^{-1}$$

$$\text{and } k(\text{SiF}_4) = 4\pi^2 \cdot (30.3 \cdot 10^{12} \text{ s}^{-1})^2 \cdot 1.66 \cdot 10^{-23} \text{ g} \quad k(\text{CF}_4) = 602 \text{ Nm}^{-1}$$

The force constants of the two compounds are almost identical.

15.2 The heats of formation and the force constants do not match. They are not expected to match, since the initial states of the compounds need to be taken into account. In addition, the vibrational force constant describes the potential just in the vicinity of the zero point but not far away from it.

15.3 Taking into account the heat of vaporization, we obtain the heats of formation of CF_4 and SiF_4 from C and Si vapours of -1939 kJmol^{-1} and -2054 kJmol^{-1} . This is the reason why we can assume a similar shape of the energy curve of breaking the bonds between C and F and between Si and F, since the extrapolation from the curvature close to the bonding distance to the rest of the curve is quite good.

<http://www.ansyco.de/IR-Spektren>

Solution problem 16: Spectroscopy in Bioorganic Chemistry

Mass spectrometry: <http://masspec.scripps.edu/information/intro/>

IR spectroscopy: <http://www.chem.ucla.edu/~webspectra/irintro.html/>

NMR spectroscopy: <http://chipco.chem.uic.edu/web1/ocol/spec/NMR.htm>

16.1 $152 \text{ g} \cdot \text{mol}^{-1}$

The molecular weight corresponds to the peak with the highest m/z in the mass spectrum. The smaller peak at $153 \text{ g} \cdot \text{mol}^{-1}$ is due to molecules with one ^{13}C isotope (8 Carbon atoms \cdot 1% ^{13}C isotopes in nature \approx 8% of the total signal at $152 \text{ g} \cdot \text{mol}^{-1}$).

16.2 $\text{C}_8\text{H}_8\text{O}_3$

$$n(\text{H}) = 2 \cdot m(\text{H}_2\text{O}) / M(\text{H}_2\text{O}) = 2 \cdot 2.37 \text{ g} / 18.02 \text{ g} \cdot \text{mol}^{-1} = 0.263 \text{ mol.}$$

$$n(\text{C}) = p \cdot V(\text{CO}_2) \cdot (\text{RT})^{-1} = \frac{106.3 \text{ kPa} \cdot 6.24 \text{ L}}{8.314 \text{ kPa} \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \cdot 303.7 \text{ K}}$$

$$= 0.263 \text{ mol}$$

$$n(\text{O}) = (m(\text{A}) - n(\text{H}) \cdot M(\text{H}) - n(\text{C}) \cdot M(\text{C})) / M(\text{O})$$

$$= (5.00 \text{ g} - 0.263 \text{ mol} \cdot 1.01 \text{ g} \cdot \text{mol}^{-1} - 0.263 \text{ mol} \cdot 12.01 \text{ g} \cdot \text{mol}^{-1}) \cdot (16.00 \text{ g} \cdot \text{mol}^{-1})^{-1}$$

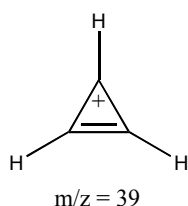
$$= 0.098 \text{ mol}$$

$$n(\text{A}) = m(\text{A}) \cdot (M(\text{A}))^{-1} \approx 5.00 \text{ g} \cdot (152 \text{ g} \cdot \text{mol}^{-1})^{-1} = 0.033 \text{ mol}$$

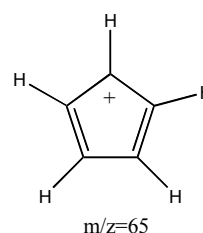
$$N(\text{O}) = n(\text{O})/n(\text{A}) = 3 \quad N(\text{H}) = n(\text{H})/n(\text{A}) = 8 \quad N(\text{C}) = n(\text{C})/n(\text{A}) = 8$$

16.3

B: C_3H_3^+



C: C_5H_5^+



Note that for $m/z=39$ only one fragment that has the molecular formula $C_3H_3^+$ will be chemically meaningful, if the molecule only contains C, H, and O. The same is true for $m/z=65$ and $C_5H_5^+$ and if it has to contain $C_3H_3^+$.

Both fragments are typical of benzenes. Other (non-cyclic) structures of those fragments should also be considered as correct solutions, if they are chemically meaningful.

- 16.4 O–H, C–H for the signals around 3200 cm^{-1} ,
 C=O, benzene for the signals around 1700 cm^{-1} ,
 the O–H group is involved in a (intra-molecular) hydrogen bond.

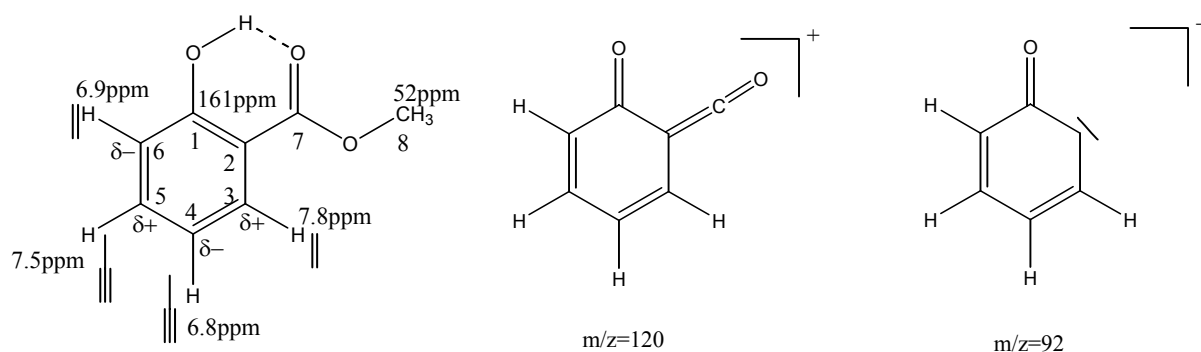
(Since it is impossible to distinguish between the signals within these two groups without additional information, the following is not thought to be part of the solution:

Broad peak at 3200 cm^{-1} : C–H Sharp peak at 2900 cm^{-1} : O–H
 Broad peak at 1700 cm^{-1} : C=O Sharp peaks around 1600 cm^{-1} : benzene)

- 16.5 4.0 ppm: OCH_3 , 6.5 – 8.0 ppm: C_6H_4 , 10.8 ppm: OH

- 16.6 52 ppm: CH_3 , 170 ppm: C=O, 110 – 165 ppm: C_6H_4
 This information can directly be obtained from the chemical shift tables.

- 16.7 Methylsalicylate.

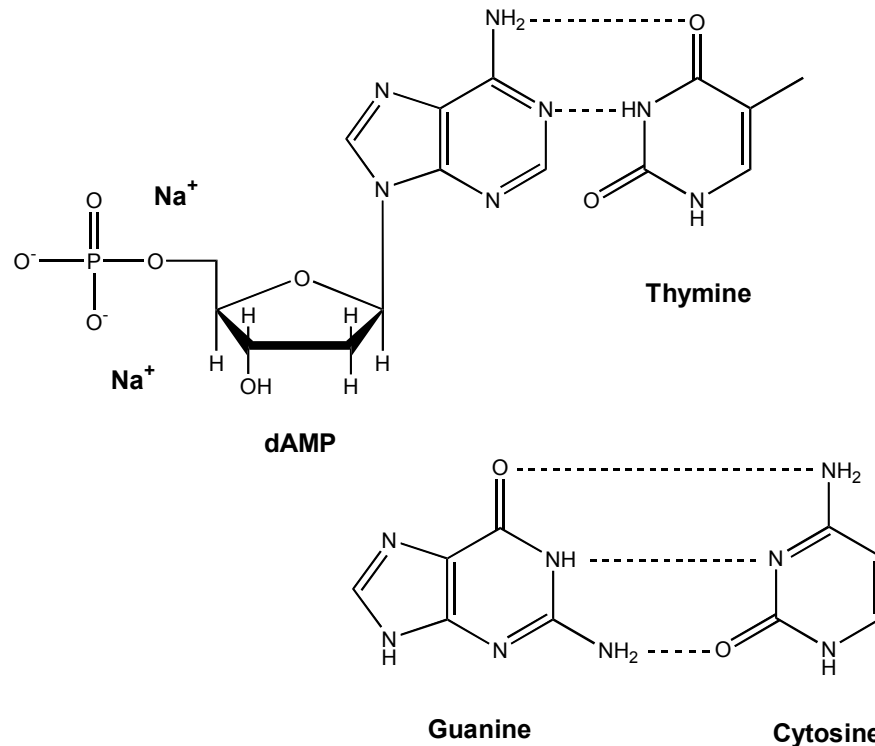


The intra-molecular hydrogen bond in the figure explains the low wavelength of the O–H band. It defines the *ortho*-position of the substitution as well as the fine splitting of the 1H signals of the aromatic system. The relative large chemical shifts of the carbon atoms C-8 and C-1 at 52 ppm and 161 ppm are explained by a $-I$ effect of the oxygen they are bond to. The assignment of the hydrogen chemical shifts in the aromatic ring is done in the following way: $\pm M$ effects define an alternating scheme of positive and negative partial charges at the aromatic ring. H-6 and H-4 have lower chemical shifts than H-5 and H-3. H-4 and H-5 have two neighbouring hydrogen atoms. Their signals are triplets that are shown in the figure. H-3 and H-6 have only one neighbouring hydrogen atom each. Their signals are doublets. All four signals are uniquely assigned by this information. The signals at $m/z=120$ and $m/z=92$ are caused by loss of CH_3-OH (Methanol) or rather CH_3-COOH (acetic acid).

- 16.8 Acetylsalicylic acid (Aspirin)

Solution problem 17: DNA, RNA, Proteins

17.1



17.2 RNA contains ribose instead of 2'-deoxyribose as the sugar moiety. Uracil (in RNA) takes the place of the nucleobase thymine (in DNA).

The 2'-OH group in ribose affects the stability of RNA against base-catalysed hydrolysis, which is initiated by deprotonation of the 2'-OH group and results in backbone cleavage. This 2'-OH group is missing in DNA which is therefore more stable than RNA.

17.3 Proteins

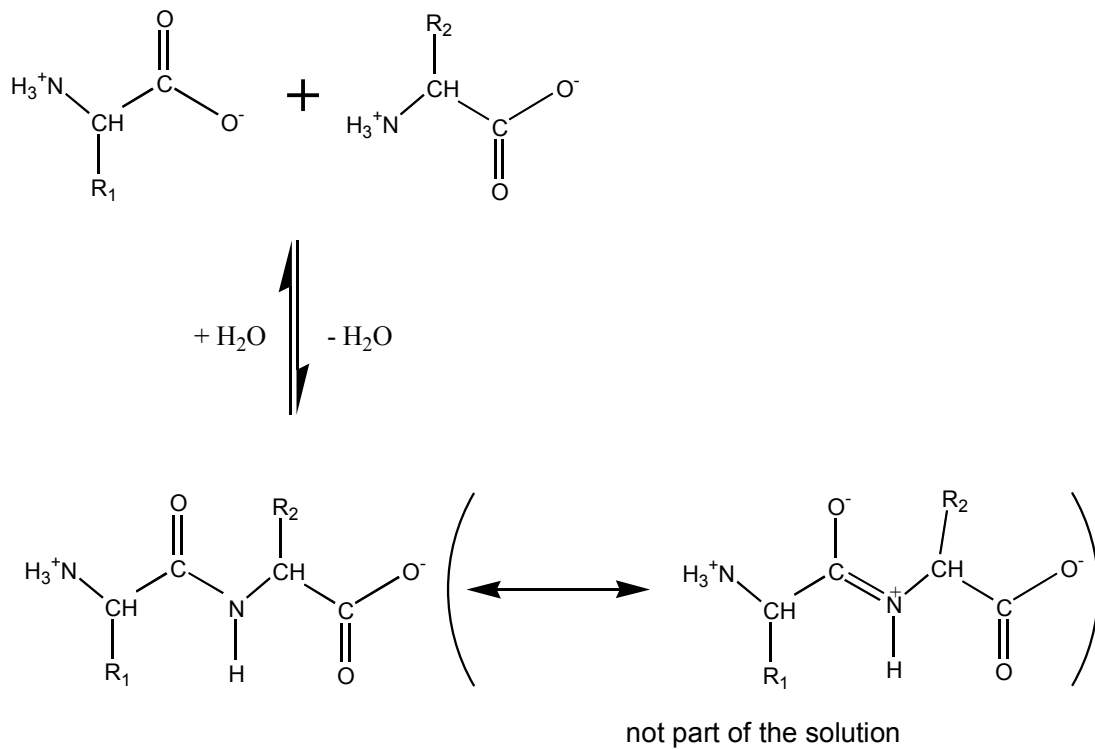
- build structures (cytoskeleton, keratin, connective tissue,...)
- generate motive forces (myosin,...)
- transport ions/small molecules (ion carriers, protein complexes,...)
- catalyse reactions (enzymes)
- fight against infections (immune response)

other answers are possible.

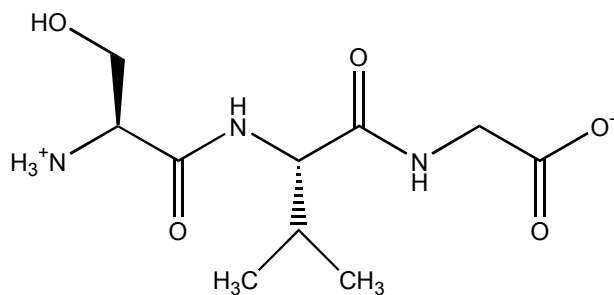
17.4 Reaction scheme of peptide formation see next page.

The peptide bond is almost planar (due to the partial double-bond as indicated in the figure). The two C_α carbon atoms are arranged in trans-configuration.

The human ribosome is a particle made up by 4 ribosomal RNA molecules and several dozen protein subunits with a total molecular weight of 4,200,000 u. It binds to the messenger RNA and, depending on the base sequence, catalyses the formation of peptide bonds between the COO⁻ group of the nascent polypeptide chain and the NH₃⁺ group of the correct activated amino acid.

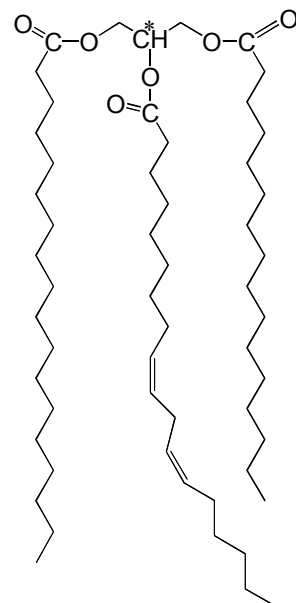


17.5 Tripeptide SVG (note the zwitterionic state):

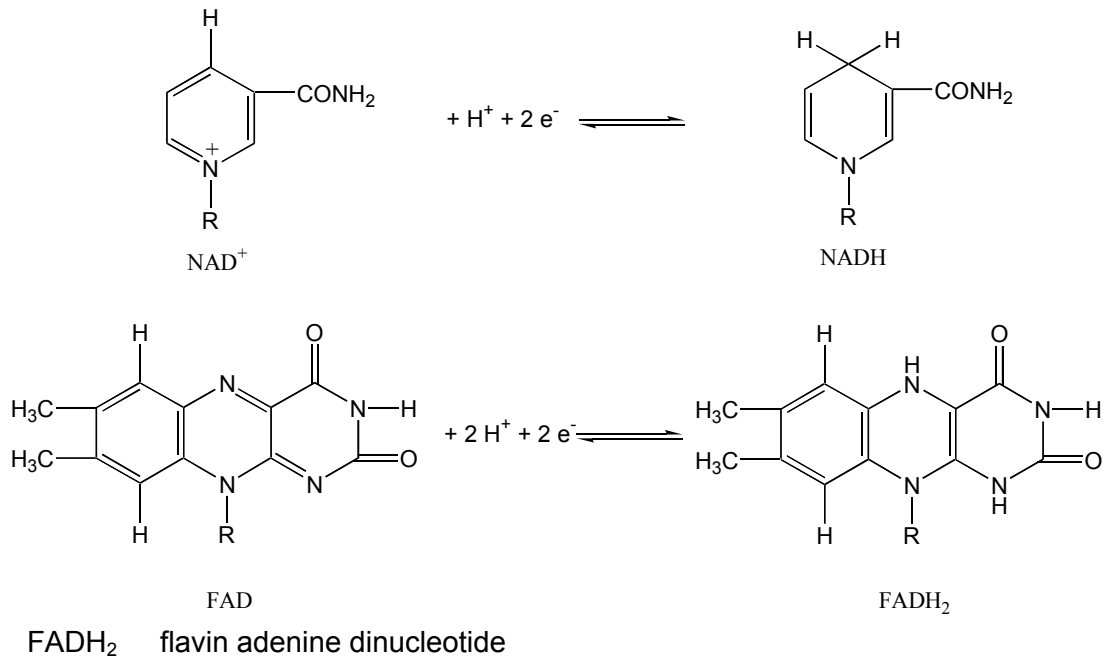


Solution Problem 18: Fatty acid degradation

18.1 Glycerol (chirality centre marked by *),
saturated or unsaturated fatty acids
e.g., stearic acid (C₁₈, position 1)
linoleic acid (C₁₈, position 2)
palmitic acid (C₁₆, position 3)



18.2 NADH nicotinamide adenine dinucleotide



18.3 Krebs-cycle; alternative names are: citric acid cycle or tricarboxylic acid cycle

The oxidation product is CO₂

The reduced products are NADH and FADH₂

18.4 The oxidation product is H₂O.

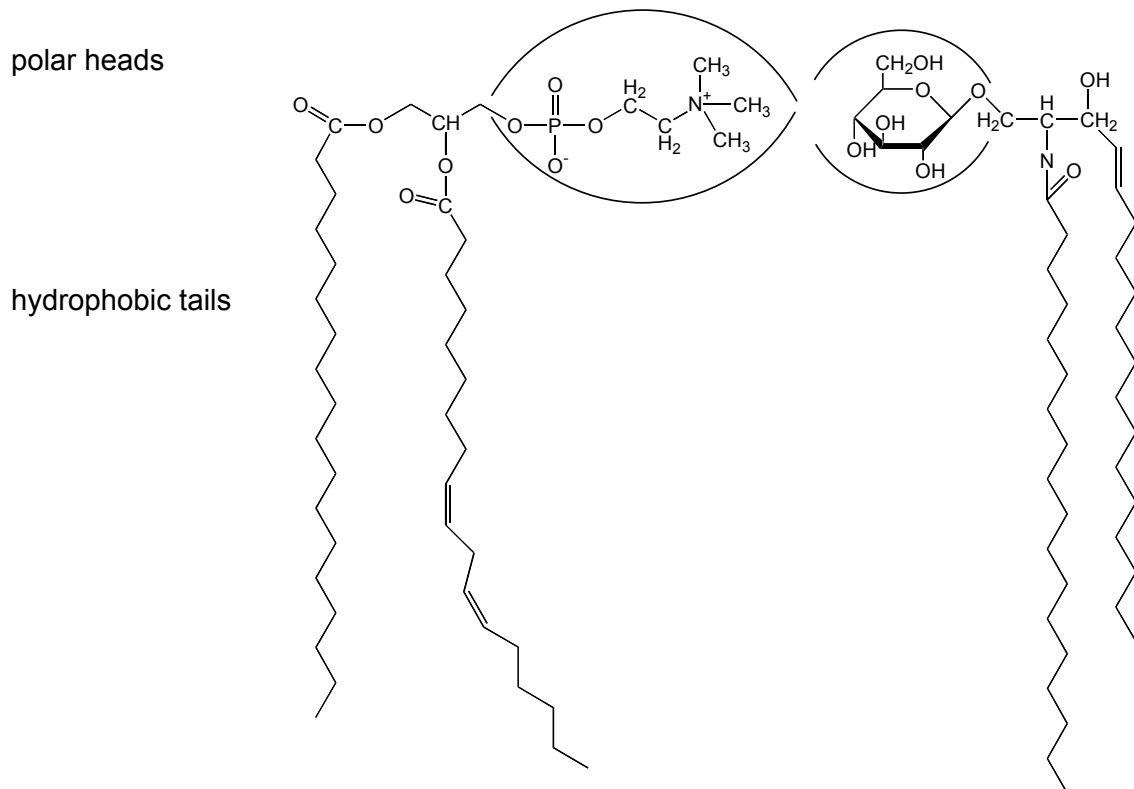
The free energy is stored at the inner mitochondrial membrane as a proton concentration gradient across the membrane. The re-entry of protons into the mitochondria causes ATP synthesis, catalysed by the enzyme ATP-synthase involving a unique rotary mechanism.

18.5 e.g. for palmitic acid: $C_{16}H_{32}O_2 + 23 O_2 \longrightarrow 16 CO_2 + 16 H_2O$

NADH and FADH₂ are electron carriers – they carry redox equivalents from the β-oxidation and the Krebs cycle to the respiratory chain.

Solution Problem 19: Lipids

19.1 Glycerol, phosphate, choline, 2 fatty acids (in this case stearic and linoleic acid)



19.2 Micelles and vesicles (lipid monolayers, lipid bilayers).

Micelles: spheroidal with (hydrophilic) head groups facing outwards; diameter depends on tail lengths, no water inside.

Vesicles: spheroidal lipid bilayers with head groups facing inwards and outwards, filled with water.

Micelles will form if the polar head group of the lipid has a much larger cross section than the hydrophobic part. Naturally occurring phospholipids carry two bulky fatty acids which do not fit into a micelle, therefore a vesicle (a lipid bilayer) forms.

19.3 The polar head groups from the outer layer of the membrane would have to cross the hydrophobic part of the membrane bilayer surrounding the cell to reach the more stable symmetric arrangement. This so-called "flip flop" mechanism has a high activation energy preventing the rearrangement of the cerebroside molecules into a symmetric distribution.

19.4 The peak at about 273 K indicates the phase transition from ice to water. The peak at about 335 K results from a phase transition of the phosphatidyl choline in the vesicles: At low temperatures, in the so-called liquid-crystalline phase, the C-C bonds of the hydrocarbon chains of the saturated fatty acids are in the single-trans conformation leading to a rigid, highly ordered array of many straight chains. Above the transition temperature, this order is disturbed by kinks in the hydrocarbon chains due to different conformations in some of the C-C bonds leading to a more disordered, fluid phase of the vesicles.

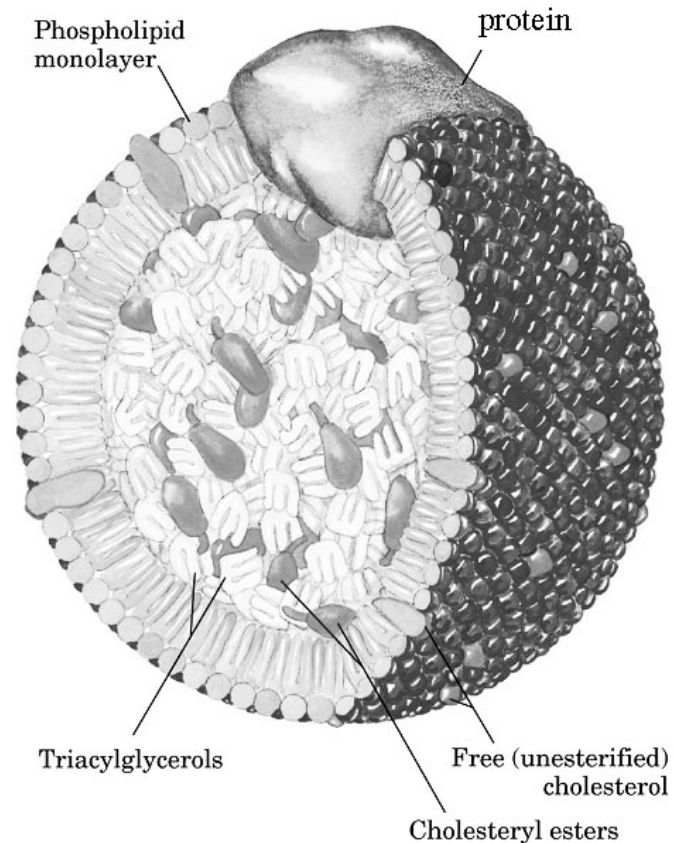
The fluidity of biological membranes is well controlled. Cells can reduce the transition temperature by introducing lipids with shorter fatty acids or with unsaturated fatty acids (the naturally occurring *cis*-conformation leads to a kink and disrupts the order). The incorporation of cholesterol, which prevents the packing of hydrocarbon chains of the other lipids is another way to control the phase of the membrane.

19.5 Lipoproteins are supramolecular structures of lipids and proteins forming micelles with the polar surfaces of the proteins and the head groups of the polar lipids (phospholipids, free cholesterol) facing outwards. The apolar lipids (triacylglycerols, cholesteryl esters) together with the hydrophobic surfaces of the proteins and the hydrophobic part of the polar lipids are hidden in the interior.

a) The OH-group of cholesterol represents the polar head group and faces outwards, the apolar steroid ring system faces inwards.

b) Cholesteryl esters are hydrophobic lipids buried in the interior of the lipoproteins.

Structure of a lipoprotein
(adapted from Lehninger,
Biochemistry)



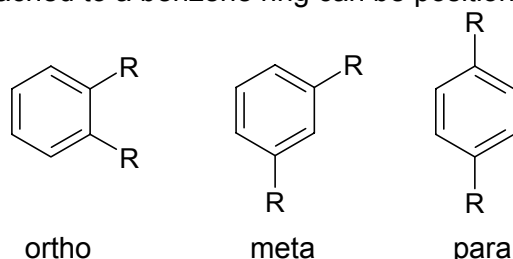
Solution problem 20: Kekulé, Benzene and the Problem of Aromaticity

20.1 Kekulé originally suggested two equilibrating structures with alternating single and double bonds. According to Kekulé, the single bonds would be longer than the double bonds and the structures would have irregular hexagonal shapes. Spectroscopy, however, has shown that benzene has a planar ring, with all the carbon-carbon bond distances having the same length of 1.397\AA (C-C typically 1.48\AA , C=C typically 1.34\AA). Since there are equal distances between the atoms, and the locations of the π

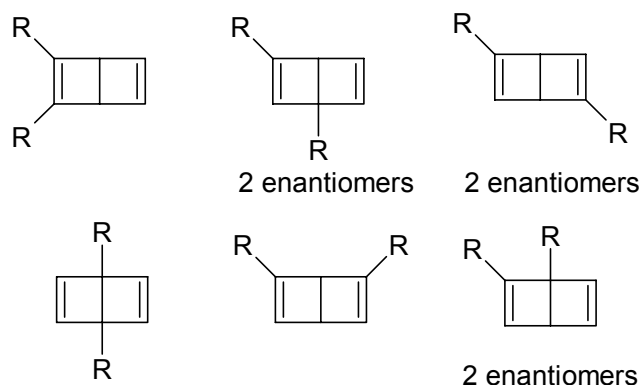
electrons in the two Kekulé structures are the only difference, they are in fact resonance structures.



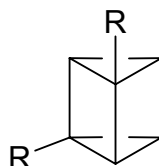
20.2 Two substituents attached to a benzene ring can be positioned in three different ways:



20.3 Dewar benzene was one of the structures proposed for benzene in the early days of organic chemistry. There are six different structural isomers of a disubstituted Dewar benzene, three of them are chiral and occur in two enantiomeric forms. Because only three benzene isomers $C_6H_4R_2$ have been found by experiment, the Dewar benzene structure cannot be correct. However, Dewar benzene can be synthesized but it is much less stable than benzene because of its considerable angle strain and its lack of aromatic stabilization.



20.4 The missing fourth isomer is an enantiomer of one of the structures that Ladenburg originally suggested. So he did not notice that one of his proposed structures is chiral.



20.5 The free enthalpies of reaction $\Delta_r G$ can be calculated from the equilibrium constant K according to the following equation:

$$\Delta_r G = -RT \cdot \ln K$$

$$K_b = 4.9 \text{ (mol/L)}^{-1}$$

$$\Delta_r G_b = -3.964 \text{ J} \cdot \text{mol}^{-1}$$

$$K_n = 970 \text{ (mol/L)}^{-1}$$

$$\Delta_r G_n = -17.154 \text{ J} \cdot \text{mol}^{-1}$$

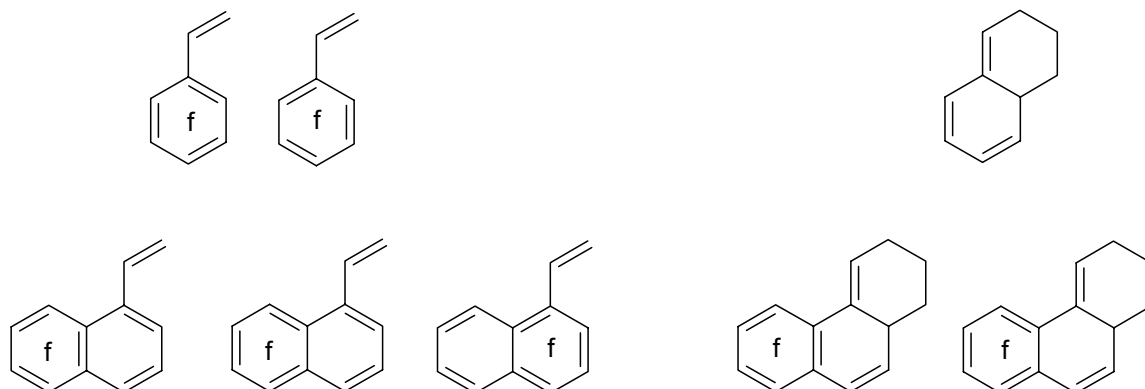
20.6 $\Delta_r G = \Delta_r H - T \cdot \Delta S$

$$\Delta_r H_b = -41.464 \text{ J} \cdot \text{mol}^{-1}$$

$$\Delta S_b = \Delta S_n = -125 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

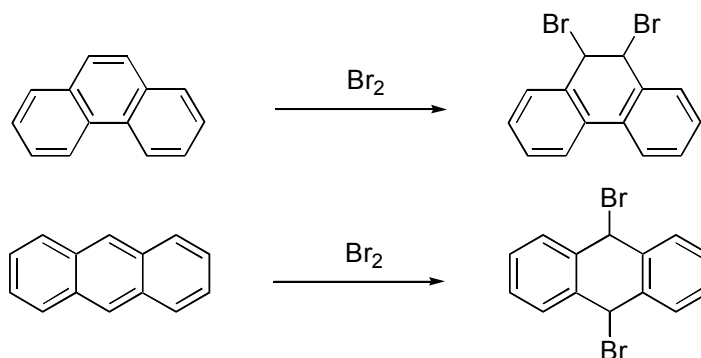
$$\Delta_r H_n = -54.654 \text{ J} \cdot \text{mol}^{-1}$$

20.7 In this Diels-Alder reaction, the aromatic π -system of styrene is completely destroyed. The product is not aromatic any more. Consequently, this loss in aromatic stabilization reduces the reaction enthalpy $\Delta_r H$. Vinyl naphthalene makes the resulting product still be aromatic, only a part of the aromatic system is destroyed. Hence, the energetic loss in this case is less than compared to styrene (naphthalene is not twice as stable as benzene) and the reaction is therefore more exothermic.

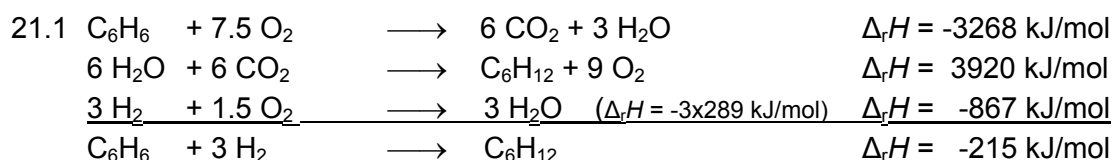


f: favourable mesomeric benzene substructure

20.8 Bromine is electrophilically added to the (formal) middle double bond in the phenanthrene molecule. In anthracene, it is added to the opposing carbon atoms. These products contain two aromatic benzene rings. The aromatic stabilization is hence larger than in the alternative products with naphthalene rings.



Solution problem 21: Benzene and cyclohexane



21.2 Making use of the enthalpy of hydrogenation of cyclohexane, the approximate value for a six-membered ring with three double bonds is

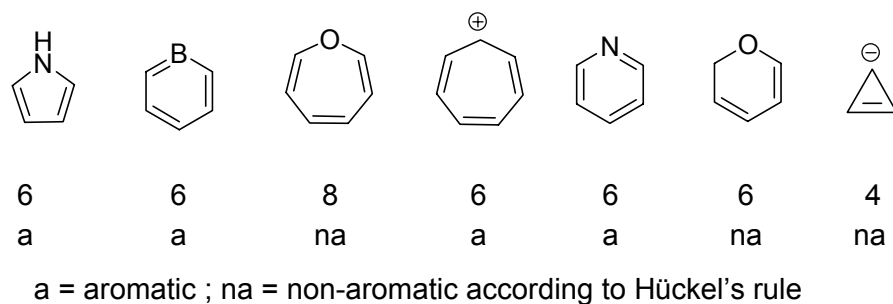
$$3 \cdot (-120 \text{ kJ mol}^{-1}) = -360 \text{ kJ mol}^{-1}.$$

Thus aromatic benzene is more stable compared to a compound with three double bonds by a difference in enthalpy of hydrogenation of

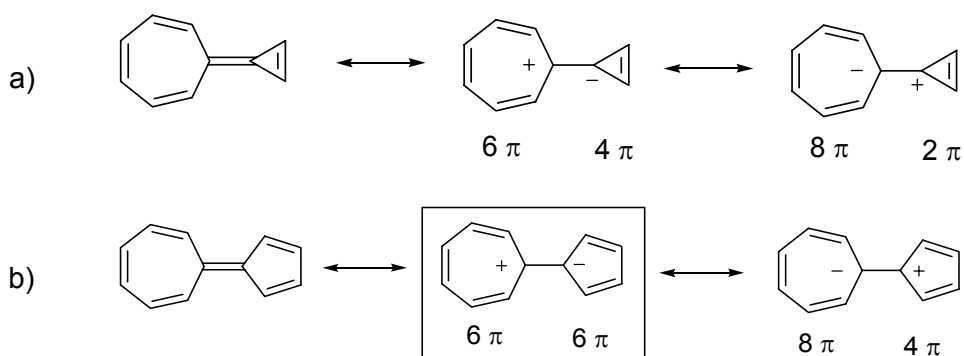
$$- (360 - 215) \text{ kJ mol}^{-1} = -145 \text{ kJ mol}^{-1}, \quad \text{resonance energy or delocalization energy.}$$

Solution problem 22: Non-Benzoid Aromatic Systems

22.1 & 22.2 Each double bond and each heteroatom (O, N) with lone pairs donates 2 π -electrons as well as a negative charge. Boron or a positive charge does not donate any electrons to the π -system but provide an empty p-Orbital for delocalization.

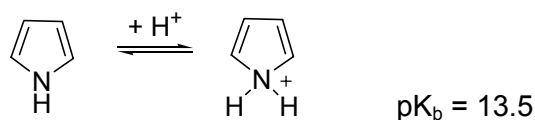


22.3

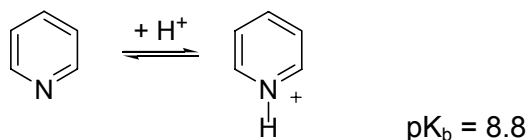


Charge separation is more favourable in compound b), because there is one mesomeric resonance structure in which both rings are formally aromatic according to Hückel's rule. In all other resonance structures at least one of the rings is formally anti-aromatic ($4n$ π -electrons). Hence, compound b) resembles electronically a cycloheptatrienyl cation fused to a cyclopentadiene anion and therefore possesses a large dipole moment.

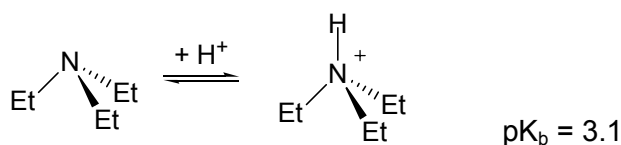
22.4



The lone pair of nitrogen in pyrrole is involved in the aromatic π -system. Protonation destroys the aromatic sextet (only 4 π -electrons left, π -system not fully conjugated any more, because the protonated nitrogen is sp^3 -hybridized). Pyrrole is hence only a very weak base.

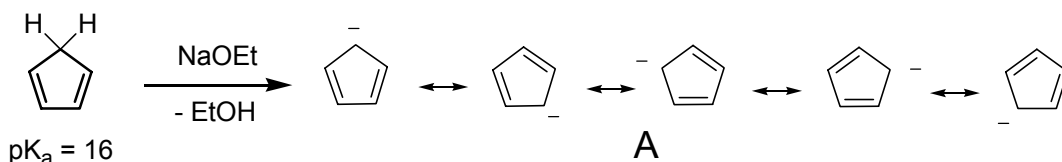


The lone pair of nitrogen in pyridine is not involved in the aromatic π -system; protonation is easier than in pyrrole. Nitrogen, however, is sp^2 -hybridized and therefore less electronegative and more difficult to protonate than in a normal amine in which nitrogen is sp^3 -hybridized.

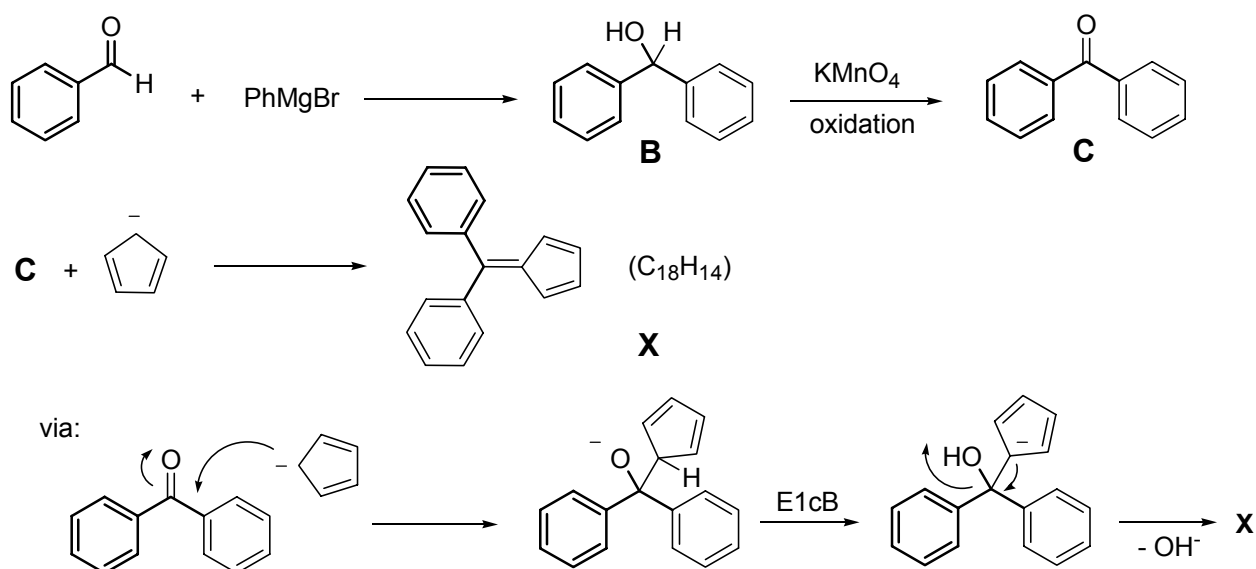


Triethyl amine is the most basic compound in this series. The higher the p-character of the lone pair, the easier is protonation.

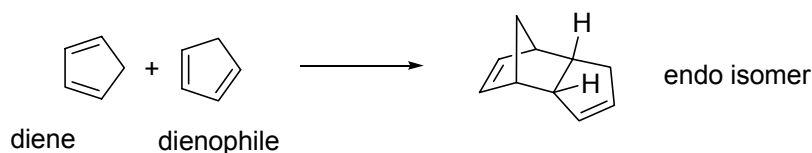
22.5 – 22.7 As a hydrocarbon, cyclopentadiene is unusually acidic ($pK_a = 16$). The increased acidity is due to the stability of the cyclopentadienide anion containing 6 π -electrons and in which the delocalization is extended over all 5 carbon atoms in complete cyclically conjugated system. Hence, the anion is aromatic. Just as in benzene, the anion is symmetric (D_{5h} -symmetry), all C-C and all C-H bonds are the same. Therefore, the ^1H nmr spectrum only shows one signal.



22.8 & 22.9 The first step in this synthesis is the nucleophilic addition of the Grignard reagent to the carbonyl group. Benzhydrol (**B**), an alcohol, forms. According to the elemental composition of **C**, **C** is the oxidation product of **B**, the ketone. This oxidation can be carried out with KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$, as there are no other oxidizable functional groups in the molecule. The cyclopentadienide anion is a potent nucleophile that adds to the carbonyl group. After the elimination of water (E1cB mechanism) it forms the corresponding fulvene derivative **X**.

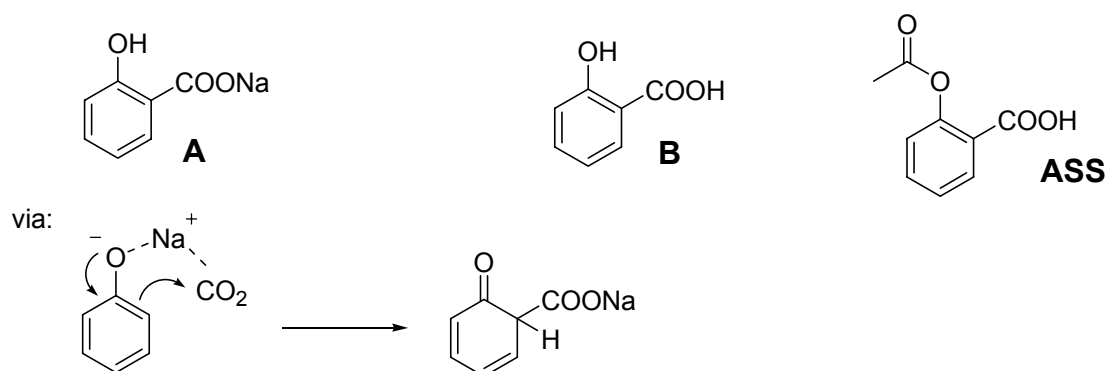


22.10 Cyclopentadiene is a 1,3-diene that easily reacts in a Diels-Alder [4+2]-cycloaddition. In this kind of reaction, it is so reactive that after a short time one molecule of 1,3-cyclopentadiene (reacting as a diene) will combine with another molecule (reacting as an olefine) to form a dimer. This bicyclic dimer is the endo adduct according to the rules of the Diels-Alder-reaction. Cyclopentadiene is not available commercially. However, the dimerization is reversible and can be reversed when the adduct is heated.



Solution problem 23: Pain Relievers

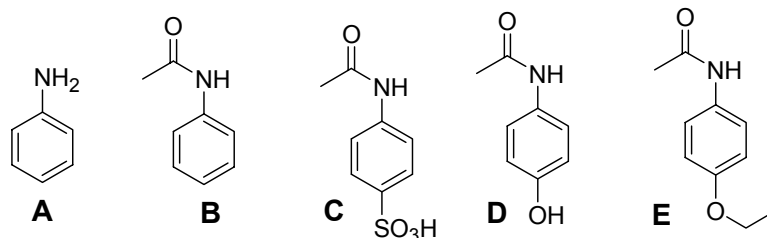
23.1 The first step is the Kolbe-Schmitt reaction in which - after protonation - salicylic acid (**B**) forms. The reaction with acetic anhydride results in the formation of acetylsalicylic acid **ASS**.



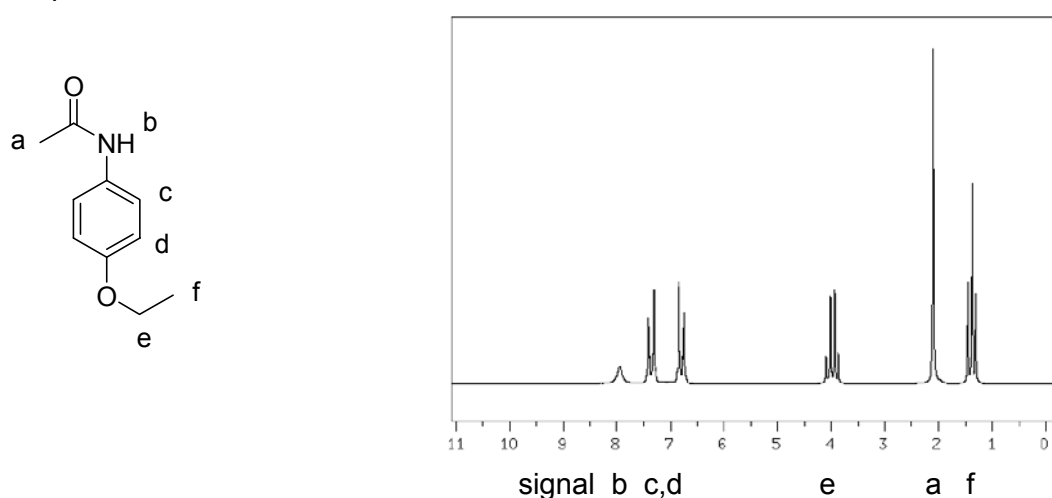
23.2

	true	false	no decision possible
ASS is more soluble in water at a pH of 2 than at a pH of 9 (The anion (pH = 9) is more soluble than the acid)	<input type="checkbox"/>	X	<input type="checkbox"/>
A further electrophilic substitution will occur ortho to the COOH group. (COOH directs meta and OAc para ⇒ attack at C4)	<input type="checkbox"/>	X	<input type="checkbox"/>
The conjugate base is less water soluble than the acid (the carboxylate is negatively charged and hence more polar and soluble)	<input type="checkbox"/>	X	<input type="checkbox"/>
The NMR spectrum shows only two CH signals in the aromatic region. (ASS shows 4 CH signals)	<input type="checkbox"/>	X	<input type="checkbox"/>
The ¹ H NMR in D ₂ O/DMSO mixtures shows 5 signals. (The COOH proton is exchanged for D)	X	<input type="checkbox"/>	<input type="checkbox"/>

23.3 There is the following reaction sequence: reduction of the nitro group to the amine (**A**), acylation (**B**) and sulfonation in the para position to form **C** (ortho substitution is not consistent with the symmetric NMR, because that would require 4 CH signals (see spectrum)). The reaction with NaOH under harsh conditions results in the formation of the phenol **D** which is finally alkylated to ether **E** (Williamson ether synthesis).



NMR spectrum:



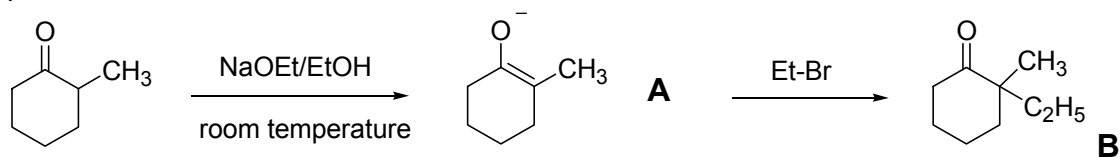
An unambiguous assignment of c and d is not possible from the given NMR spectrum.

23.4

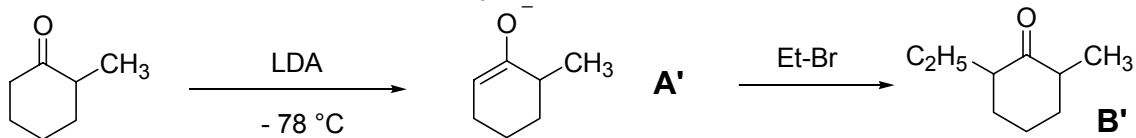
	true	false	no decision possible
At pH = 9 phenacetin is more polar than acetylsalicylic acid (<i>ASS can be deprotonated to form an anion, phenacetin not</i>)	<input type="checkbox"/>	X	<input type="checkbox"/>
Both compounds can be deprotonated by NaHCO ₃	<input type="checkbox"/>	X	<input type="checkbox"/>
The aromatic ring in phenacetin is more electron rich than in acetylsalicylic acid (<i>two donor substituents, ASS has two acceptor groups</i>)	X	<input type="checkbox"/>	<input type="checkbox"/>
None of them is chiral.	X	<input type="checkbox"/>	<input type="checkbox"/>
On a silica gel TLC plate, developed with 5% acetic acid in ethyl acetate, the R _f value for phenacetin is larger than for acetylsalicylic acid. (<i>ASS is more polar than E, hence has a lower R_f</i>)	X	<input type="checkbox"/>	<input type="checkbox"/>

Solutions problem 24: Carbonyl Chemistry

24.1



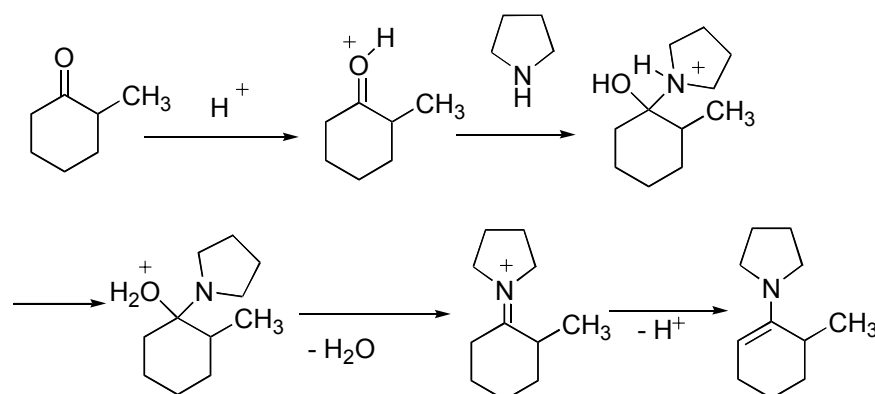
reversible deprotonation, thermodynamic control, more substituted enolate forms



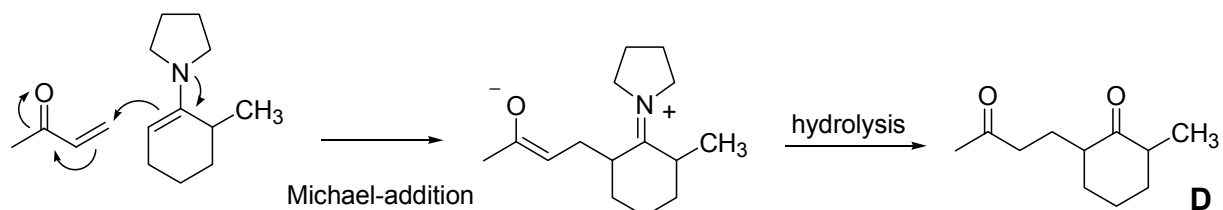
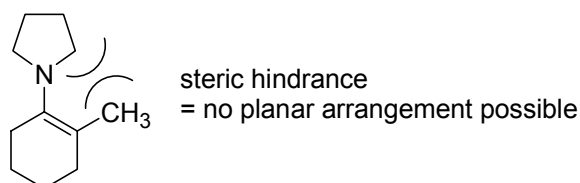
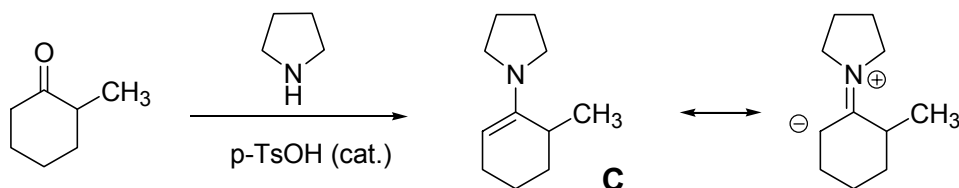
irreversible deprotonation, kinetic control, the more acidic proton is removed, less substituted enolate forms

24.2 BuLi can also act as a nucleophile and attacks the carbonyl C-atom. Therefore a non-nucleophilic base such as LDA has to be used.

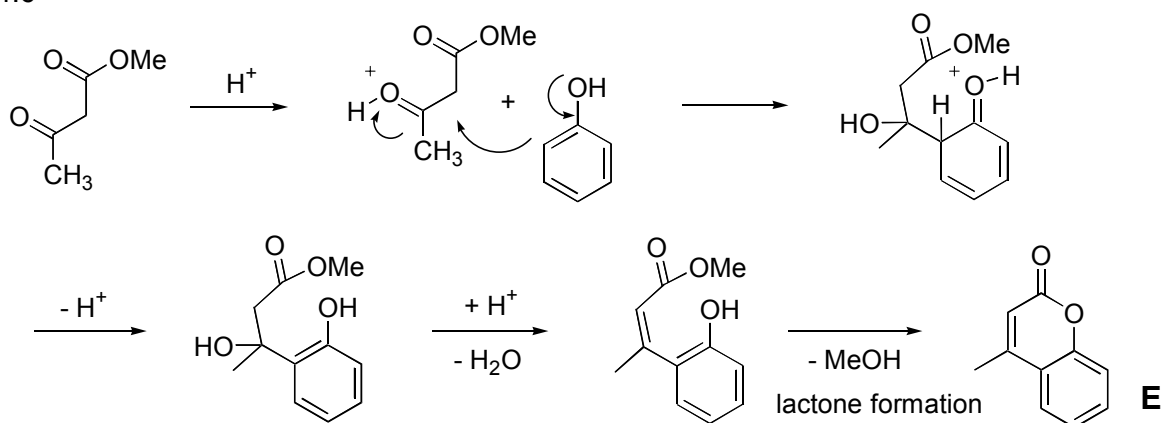
24.3 – 24.5 Formation of the enamine.



Enamines are nucleophilic, because the nitrogen lone pair transfers electron density to the β -carbon (see resonance structure on the right side).

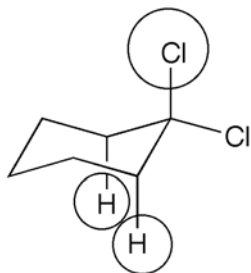


24.6



Solution problem 25: Cyclohexanes

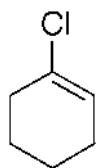
25.1

**A**

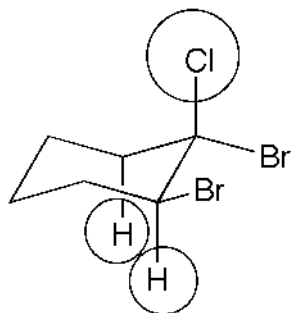
The chair is the most stable conformation of a cyclohexane ring. Large substituents prefer the equatorial position.

In an elimination reaction of an E2 type, the groups that are eliminated must have antiperiplanar positions. This is only possible in a chair conformation if both groups are in axial positions.

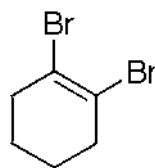
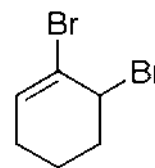
25.2

**B**

25.3

**C**

25.4

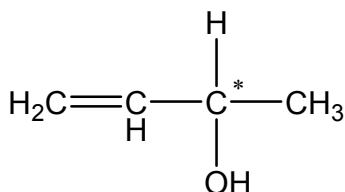
**D****E**

Because of the electron-attracting effect of bromine, the proton of a carbon that is bound to a bromine substituent, becomes more acidic. This proton is therefore removed more easily by a base and **D** becomes the major product.

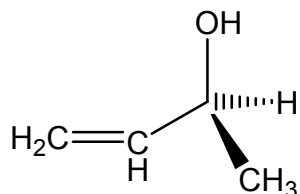
Solution Problem 26: Chiral Compounds

There are five molecules with asymmetric C atoms – three of them have one chiral centre and two of them have two chiral centres. One of the latter is symmetric so that there is a meso- compound.

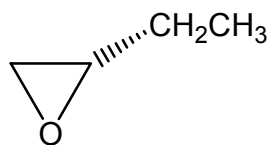
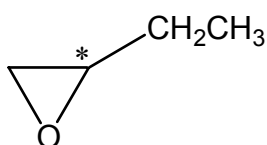
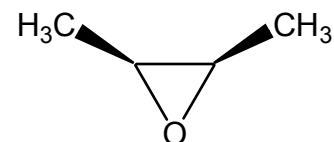
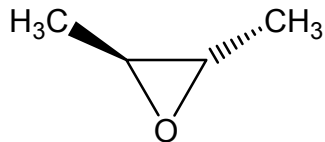
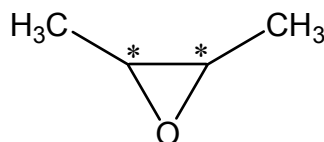
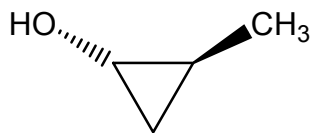
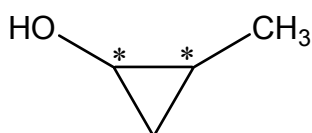
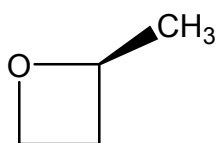
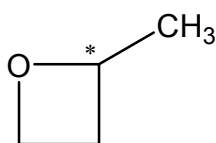
26.1



26.2

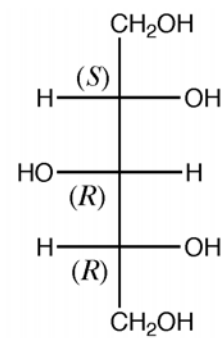
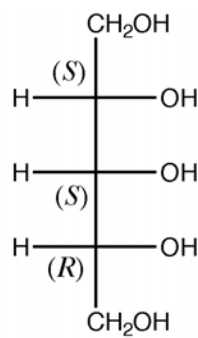
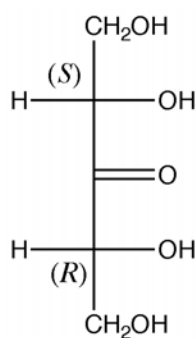


26.3



Solution Problem 27: Monosaccharides

27.1 & 27.2.



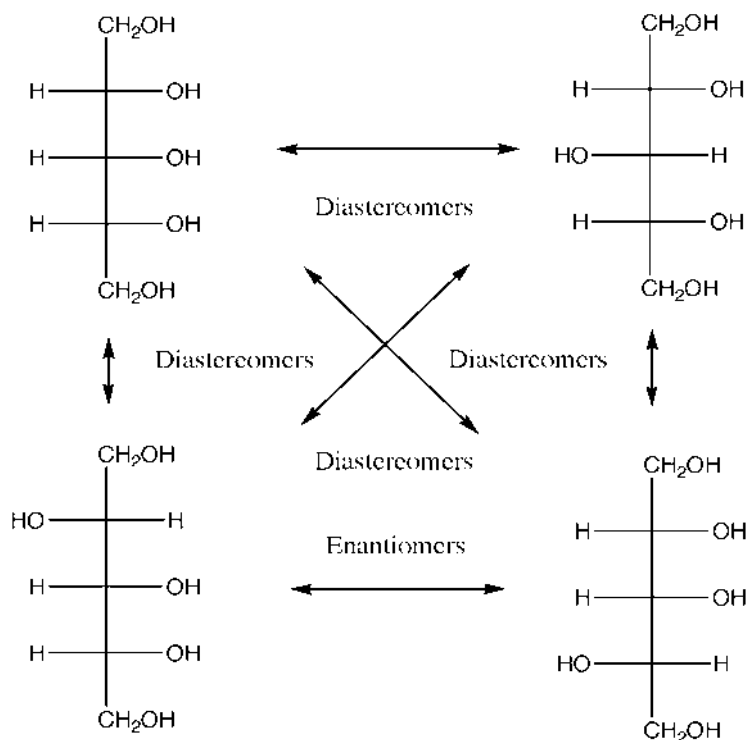
A

B

C

A monosaccharide has the general formula $C_n(H_2O)_n$. Consequently, a molecular weight of 150 Da can only be reached by the formula $C_5(H_2O)_5$. After reduction, **B** and **C** are the only two possible products that are optically inactive. These two products can only be formed from **A** as the common precursor. If two groups only differ in chirality, the (*R*)-center has a higher priority than the (*S*)-center.

27.3

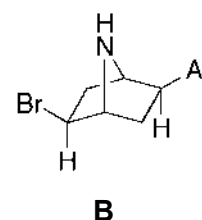
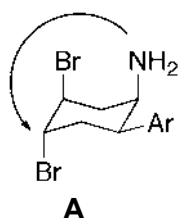
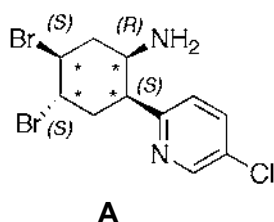


Solution Problem 28: Epibatidine

28.1 & 82.2

28.3

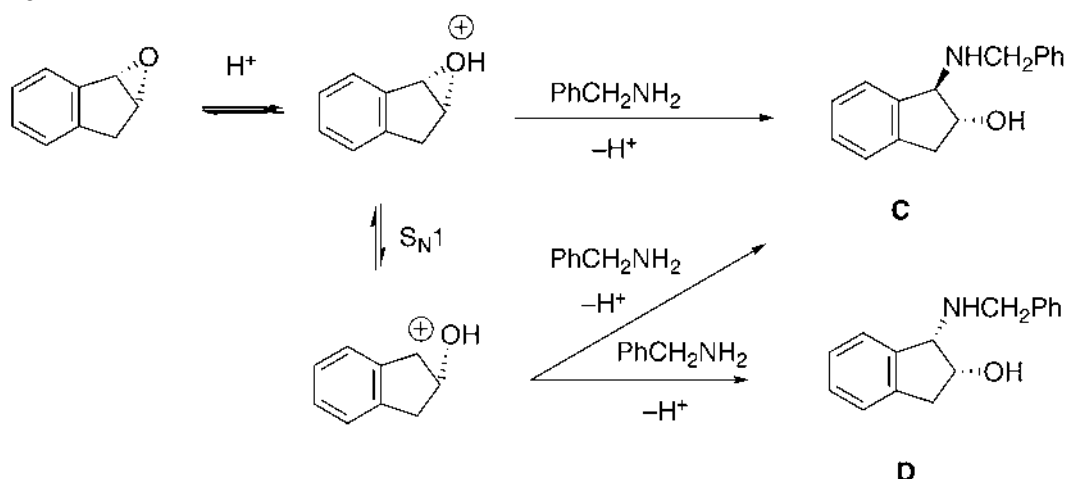
28.4



In a nucleophilic substitution (S_N2), the nucleophile attacks the reaction centre at the back side with respect to the leaving group. In order to reach the reaction centre, the nucleophilic group (amino group) must take an axial position and subsequently replaces the bromine atom that points away from the incoming nucleophilic group.

Solution problem 29: Crixivan®

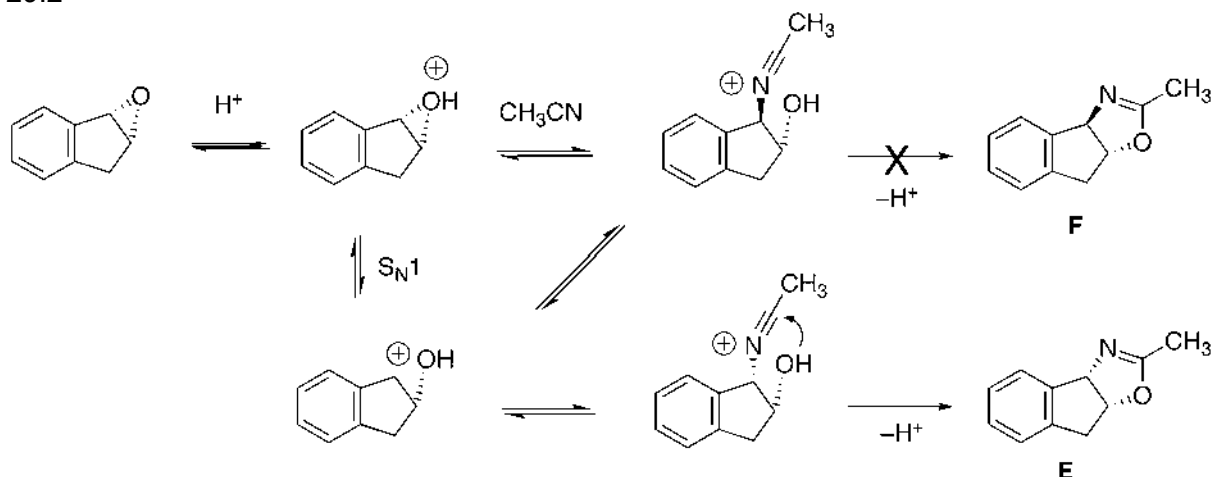
29.1



Formation of **C** (S_N2 pathway): back side attack on benzylic position; the positive charge in the transition state at the reaction centre is stabilized by the phenyl group.

Formation of **C** and **D** (S_N1 pathway): regioselective opening at the benzylic position due to resonance stabilization of the resulting carbocation by the phenyl group.

29.2



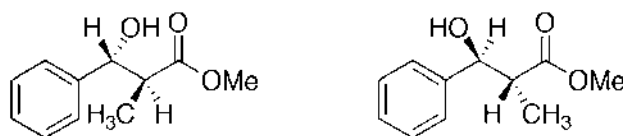
Only the cis-anellated product **E** can form. The trans-anellated compound **F** can not form from two five membered rings because of severe ring strain.

Solution problem 30: Stereoselective Reduction

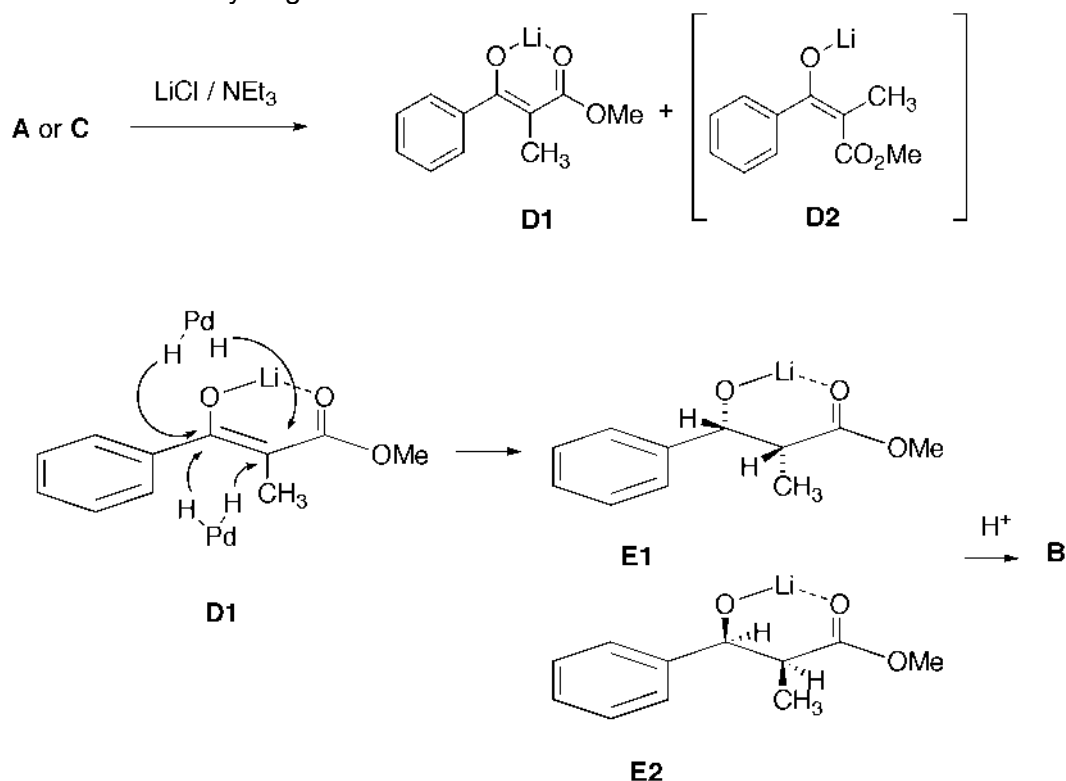
30.1 enantiomers of B



30.2 enantiomers of B*



30.3. stereoselective hydrogenation



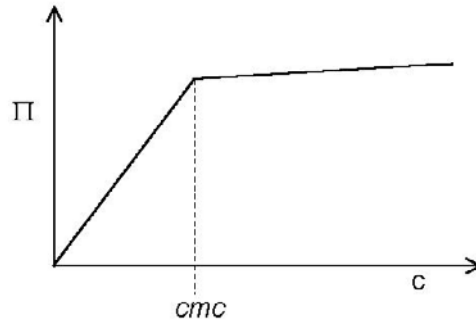
Obviously, **A** and **C** must be reduced by a common, achiral intermediate, since **C** is racemized in the process. The racemization of **C** can be understood by the formation of the enolate **D1**, which forms with a higher preference than **D2**, because of the strong chelation effect of Li^+ present as an additive in the reaction mixture. The donation of hydrogen by the metal in the usual way (syn-addition) from the top or the bottom of **D1** leads to racemic **E1/E2** as single diastereomers. Hydrolysis leads to racemic **B**.

Solution Problem 31: Surfactant Micelles

31.1 The cmc is $c = 0.75 \text{ gL}^{-1}$.

31.2 Amphiphilic molecules contain a hydrophilic part which is "water-soluble" and a hydrophobic part which is "water insoluble", i.e. the free energy for the dissolution of the hydrophilic part in water is negative, while it is positive for the hydrophobic part. When micellar aggregates are formed, exposure of hydrophobic parts of the molecule to the aqueous phase is avoided ("hydrophobic interaction"). In addition, hydrophilic head groups can interact with water (negative hydration energy).

31.3



31.4

a) $K = \frac{c(B)}{c(A)^N}$ and $c(A) + N \cdot c(B) = c_0$

relationship: $K = \frac{c_0 - c(A)}{Nc(A)^N}$

b) When $c(A) = f \cdot c_0$, $c(A) = \left(\frac{1-f}{fNK} \right)^{\frac{1}{N-1}}$

f	0.9999	0.5	0.01	$1 \cdot 10^{-3}$	10^{-4}
c(A) · mol ⁻¹ L	0.011	0.013	0.015	0.015	0.016
c ₀ · mol ⁻¹ L	0.011	0.027	1.477	15.481	162.265
N c(B) · mol ⁻¹ L	$1.11 \cdot 10^{-6}$	0.013	1.462	15.466	162.249
c(B) · mol ⁻¹ L	$2.23 \cdot 10^{-8}$	$2.69 \cdot 10^{-4}$	0.029	0.309	3.245

31.5 a) For spherical aggregates with radius l and aggregation number N , micelle volume V and micelle surface A are:

(I) $V = Nv = \frac{4\pi l^3}{3}$ (v = volume of surfactant molecule)

(II) $A = Na = 4\pi l^2$ (a = head group area of surfactant molecule)

division of (I) by (II): $\frac{v}{a} = \frac{l}{3}$ or $\frac{v}{al} = \frac{1}{3}$

b) For cylindrical aggregates with radius l we consider a part of the cylinder with length b and the aggregation number N . Micelle volume V and micelle surface A are:

(I) $V = Nv = \pi l^2 b$

(II) $A = Na = 2\pi l b$

division of (I) by (II): $\frac{v}{a} = \frac{l}{2}$ or $\frac{v}{al} = \frac{1}{2}$

c) For a flat bilayer with the thickness $2l$ we consider a part of the size (area) x and aggregation number N . Micelle volume V and micelle surface A are:

(I) $V = Nv = x \cdot 2l$

(II) $A = Na = 2x$

division of (I) by (II): $\frac{v}{a} = l$ or $\frac{v}{al} = 1$

$$31.6 \text{ a) } \frac{v}{al} = \frac{0.35 \text{ nm}^3}{0.57 \text{ nm}^2 \cdot 1.67 \text{ nm}} \quad \frac{v}{al} = 0.37$$

$\frac{v}{al} > \frac{1}{3}$ cylindrical micelles form (note: slightly elongated micelles, "short cylinders")

for $\frac{1}{3} < \frac{v}{al} < \frac{1}{2}$, cylindrical micelles form.

The value calculated for the spherical geometry is an upper value. Concerning larger values of the packing parameter, the volume of the hydrophobic part of the molecule is too large to fit into a sphere. Cylinders (or slightly elongated micelles) can form, although the geometric conditions are not ideal. (Note also that the surfactant length given refers to the maximum extension of the hydrocarbon chain: conformations with shorter extensions may form, but there is no conformation with longer lengths.)

b) Spherical micelles. Note: After the addition of a base, protolysis increases, the charges on the head groups (on average) increase and thus the effective head group area increases (electrostatic repulsion). Hence, the value of the packing parameter $v \cdot (a)^{-1} = 0.37$ calculated in a) decreases. Since 0.37 is not much higher than the limit for spherical micelles, the regime of spherical aggregates can be reached.

Solution Problem 32: Self-Assembly of Amph. Block Copolymers

32.1

	in water	in toluene
I	spherical micelles	phase separation
II	phase separation	spherical micelles

$$32.2 \quad M(\text{PVP-monomer}) = 105.15 \text{ g mol}^{-1} \quad M(\text{PS-monomer}) = 104.16 \text{ g mol}^{-1}$$

$$M(\text{A}) = 15125.97 \text{ g mol}^{-1} \quad M(\text{B}) = 17439.27 \text{ g mol}^{-1}$$

The molar mass of the micelles $M(\text{micelle})$ can be obtained from the osmosis experiment. Notice that the molar concentration c_{mo} (mol L^{-1}) refers to the mass concentration c_{ma} (g L^{-1}):

$$c_{\text{mo}} = \frac{c_{\text{ma}}}{M(\text{micelle})} \quad \text{and} \quad c_{\text{mo}} = \frac{n}{V}, \quad n = c_{\text{mo}} \cdot V$$

$$\Pi V = nRT \quad \Pi V = c_{\text{mo}} \cdot V RT$$

$$M(\text{micelle}) = \frac{c_{\text{ma}} RT}{\Pi} M(\text{micelle})$$

The osmotic pressure is counterbalanced by the pressure of the solvent column above the solution, thus $\Pi = \rho gh$.

$$M(\text{micelle}) = \frac{c_{\text{ma}} RT}{\rho gh}$$

$$\begin{array}{lll} \text{micelle A:} & h = 11.02 \text{ mm} & \Pi = 93.62 \text{ Pa} & M(\text{micelle A}) = 211820 \text{ g mol}^{-1} \\ \text{micelle B:} & h = 2.48 \text{ mm} & \Pi = 21.07 \text{ Pa} & M(\text{micelle B}) = 941231 \text{ g mol}^{-1} \end{array}$$

Note: In a real experiment, ideal behaviour can not be assumed. Instead, the osmotic pressures of solutions of different concentrations are measured. By extrapolation of

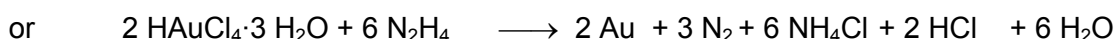
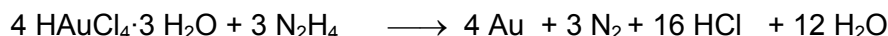
$\Pi \cdot c_{ma}^{-1}$ towards zero concentration the molar mass is obtained. Thus membrane osmometry is a convenient tool for molar mass determination of polymers and colloids.

The aggregation number N is obtained from the molar mass of the micelles and block copolymers

$$N(A) = \frac{M(\text{micelle } A)}{M(A)} = \frac{211820 \text{ g mol}^{-1}}{15125.97 \text{ g mol}^{-1}} \quad N(A) = 14$$

$$N(B) = \frac{M(\text{micelle } B)}{M(B)} = \frac{941231 \text{ g mol}^{-1}}{17439.27 \text{ g mol}^{-1}} \quad N(B) = 54$$

32.3 Reduction with hydrazine: hydrazine can react to give nitrogen or nitrogen and NH_3 .



Reduction with sodium borohydride:



32.4 $M(C) = 25224.33 \text{ g mol}^{-1}$

$M(D) = 19331.97 \text{ g mol}^{-1}$

$M(\text{micelle } C) = N \cdot M(C)$

$M(\text{micelle } D) = N \cdot M(D)$

$M(\text{micelle } C) = 7819542.3 \text{ g mol}^{-1}$

$M(\text{micelle } D) = 2377832.31 \text{ g mol}^{-1}$

$$c_{mo}(\text{micelle}) = \frac{c_{ma}(\text{polymer})}{M(\text{micelle})}$$

$$c_{mo}(\text{micelle } C) = 1.2788 \cdot 10^{-6} \text{ mol L}^{-1}$$

$$c_{mo}(\text{micelle } D) = 4.2055 \cdot 10^{-6} \text{ mol L}^{-1}$$

When $M(\text{H AuCl}_4 \cdot 3 \text{ H}_2\text{O}) = 393.84 \text{ g mol}^{-1}$ the molar concentration of $\text{H AuCl}_4 \cdot 3 \text{ H}_2\text{O}$ for the two cases a) and b) is:

a) $c_{mo}(\text{H AuCl}_4 \cdot 3 \text{ H}_2\text{O}) = 2.5391 \cdot 10^{-3} \text{ mol L}^{-1}$

b) $c_{mo}(\text{H AuCl}_4 \cdot 3 \text{ H}_2\text{O}) = 0.0127 \text{ mol L}^{-1}$

Hence, we can calculate the equivalents of $\text{H AuCl}_4 \cdot 3 \text{ H}_2\text{O}$ that have been added per micelle, i.e. the number of gold ions per micelle $z(\text{Au, micelle})$:

$$z(\text{Au, micelle}) = \frac{c(\text{H AuCl}_4 \cdot 3 \text{ H}_2\text{O})}{c_{mo}(\text{micelle})} \quad (I)$$

We obtain the gold colloid mass $m(\text{Au, colloid})$ and by its volume V the radius r and diameter d of the spherical gold colloid

$$m(\text{Au, micelle}) = \frac{z(\text{Au, micelle}) \cdot M(\text{Au})}{N_a} \quad m(\text{Au, colloid}) = m(\text{Au, micelle})$$

$$V(\text{Au, colloid}) = \frac{4}{3} \pi r^3 \quad \text{and} \quad V(\text{Au, colloid}) = \frac{m(\text{Au, colloid})}{\rho(\text{Au})}$$

$$r = \left(\frac{3 \cdot m(\text{Au, colloid})}{4 \pi \rho(\text{Au})} \right)^{\frac{1}{3}} \quad \text{and} \quad d = 2 \left(\frac{3z(\text{Au, micelle})M(\text{Au})}{4 \pi \rho(\text{Au})N_a} \right)^{\frac{1}{3}} \quad (II)$$

$M(\text{Au}) = 196.97 \text{ g mol}^{-1}$ and $\rho(\text{Au}) = 19.3 \text{ g cm}^{-3}$.

Equations (I) and (II) lead to

	polymer C a) 0.01g Au-acid	polymer C b) 0.05g Au-acid	polymer D a) 0.01g Au-acid	polymer D b) 0.05g Au-acid
z(Au, micelle)	1985	9931	604	3019
d	4.0 nm	6.8 nm	2.7 nm	4.6 nm

32.5 The surface of a gold colloid is energetically unfavourable, because the surface atoms have fewer neighbours and thus contribute less crystallization energy than inner "bulk" gold atoms (surface tension is based on the same phenomenon, so that reasoning based on surface tension is correct as well). The total surface area of larger particles is smaller. Therefore, particles tend to become as large as possible (by direct growth or coagulation) to decrease the ratio of surface area to volume.

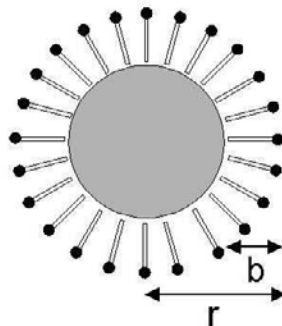
Additional notes:

1. This is the reason why e.g. metallic gold forms as a macroscopic precipitate rather than colloids if you reduce gold ions in an aqueous solution without any additives. In the block copolymer micelles, however, growth is restricted due to compartmentalization.
2. Many small gold colloids inside one micelle can form if the inner polymer block has functional groups that attach to the surface of the gold with a gain in energy: the colloids are "stabilized". If a fast reduction creates many nuclei inside one micelle, multiple small gold colloids can be stabilized. Further, small colloids are often kinetically stabilized, because the activation energy for their coagulation is higher than the thermal energy.

Solution Problem 33: Microemulsions

33.1 It's a crosslinker. The resulting particle is a small spherical polymer network.

33.2 The geometric conditions can be described as follows:



When r is the radius of the total microemulsion droplet, b the length of the surfactant molecule and $r-b$ the radius of the polymer particle, you obtain:

$$V(\text{monomer}) = \frac{4\pi(r-b)^3}{3} \quad \text{and} \quad V(\text{surfac.}) = \frac{4\pi r^3}{3} - \frac{4\pi(r-b)^3}{3}$$

$$S = \frac{m(\text{surfac.})}{m(\text{monomer})} = \frac{V(\text{surfac.})}{V(\text{monomer})} = \frac{r^3}{(r-b)^3} - 1$$

to obtain particles with diameter d and $r = 0.5 \cdot d + 2 \text{ nm}$

d	r	S
20 nm	12 nm	0.73
40 nm	22 nm	0.33
120 nm	62 nm	0.10

33.3 The surface of a spherical particle is:

$$A(\text{particle}) = A(\text{monomer droplet}) = 4\pi(r - b)^2$$

For 1 g of polystyrene, i.e. 1 cm^3 of polymer, the particle number is

$$N = \frac{1 \text{ cm}^3}{V(\text{particle})} = \frac{3 \cdot 1 \text{ cm}^3}{4\pi(r - b)^3} \quad \text{and the total surface of 1 g of polystyrene particles is:}$$

$$A(1 \text{ g polystyrene}) = N \cdot A(\text{monomer droplet}) = \frac{3 \cdot 1 \text{ cm}^3}{4\pi(r - b)^3} 4\pi(r - b)^2 = \frac{3 \text{ cm}^3}{(r - b)}$$

d	A(monomer droplet)	A(1 g of polystyrene)
20 nm	1257 nm^2	$3.0 \cdot 10^{20} \text{ nm}^2 = 300 \text{ m}^2$
40 nm	5026 nm^2	$1.5 \cdot 10^{20} \text{ nm}^2 = 150 \text{ m}^2$
120 nm	45239 nm^2	$5.0 \cdot 10^{19} \text{ nm}^2 = 50 \text{ m}^2$

33.4 c) is true, the others are false.

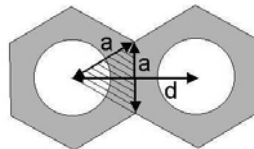
An amphiphilic enzyme should be included into the interface of the microemulsion particle. With the active centre in the hydrophilic part, it will be located towards the hydrophilic, aqueous phase and the enzyme may remain active.

Solution problem 34: Silica Nanostructures

34.1 $A = \text{Si}(\text{OCH}_3)_4$, $B = \text{Si}(\text{OH})_4$

34.2 a) Bragg: $n\lambda = 2d \cdot \sin\theta$, with $n = 1$, results see table below

$$b) \quad w = \frac{\rho(\text{surfac.}) \cdot V(\text{surfac.})}{\rho(\text{SiO}_2) \cdot V(\text{SiO}_2) + \rho(\text{surfac.}) \cdot V(\text{surfac.})}$$



$V(\text{surfac.}) = V(\text{pore})$ and $V(\text{SiO}_2)$ can be calculated for a structure of height l :

$$V(\text{pore}) = \pi r^2 l$$

$$V(\text{SiO}_2) = 6 \cdot A(\text{triangle}) \cdot l - \pi r^2 l$$

$$\text{with } A(\text{triangle}) = a \cdot \frac{1}{2} \cdot \frac{1}{2} d \quad \text{and} \quad \left(\frac{1}{2} a\right)^2 + \left(\frac{1}{2} d\right)^2 = a^2 \rightarrow a = \frac{1}{\sqrt{3}} d$$

$$V(\text{SiO}_2) = 0.5 \cdot \sqrt{3} d^2 l - \pi r^2 l$$

$$r = \left(\frac{w \cdot \rho(\text{SiO}_2) \sqrt{3} d^2}{2 \cdot (1 - w) \cdot \rho(\text{surfac.}) \cdot \pi + 2w \cdot \rho(\text{SiO}_2) \cdot \pi} \right)^{\frac{1}{2}}$$

surfactant	d	r
C ₁₂ H ₂₅ N(CH ₃) ₃ Cl	3.80 nm	1.50 nm
C ₁₄ H ₂₅ N(CH ₃) ₃ Cl	4.20 nm	1.80 nm
C ₁₆ H ₂₅ N(CH ₃) ₃ Cl	4.70 nm	2.10 nm
C ₁₈ H ₂₅ N(CH ₃) ₃ Cl	5.00 nm	2.30 nm

34.3 Increasing tail length leads to a) an increase in diameter and b) an increase in pore distance (the same total volume of surfactants but more surfactant molecules per pore, i.e. fewer pores and larger pore distances).

34.4 a) In equilibrium the rate of adsorption ($k_{ads}(n^*-n_{ads})p$) is equal to the rate of desorption ($k_{des} n_{ads}$):

$$k_{des} n_{ads} = (k_{ads}(n^*-n_{ads})p)$$

where n^* = maximum adsorbable amount (in molL⁻¹)

and n_{ads} = adsorbed amount (in molL⁻¹)

$$\frac{n_{ads}}{n^* - n_{ads}} = \frac{k_{ads}}{k_{des}} p \quad \text{or} \quad \frac{V_{ads}}{V^* - V_{ads}} = \frac{k_{ads}}{k_{des}} p \quad \text{and with} \quad \frac{k_{ads}}{k_{des}} = K$$

$$\frac{p}{V_{ads}} = \frac{1}{KV} + \frac{p}{V^*}$$

b) Linear regression of pV_{ads}^{-1} versus p yields the slope $(V^*)^{-1}$.

$$A_{sp} = \frac{n^* \cdot A(N_2)N_a}{m(\text{SiO}_2)} \quad \text{and} \quad A_{sp} = \frac{V^* p_0}{RTm(\text{SiO}_2)} A(N_2) \cdot N_a \quad \text{with} \quad m(\text{SiO}_2) = 1 \text{ g}$$

surfactant	V^* (cm ³) ⁻¹	A_{sp} (m ² g ⁻¹) ⁻¹	r (nm) ⁻¹
C ₁₂ H ₂₅ N(CH ₃) ₃ Cl	49.0	747.1	1.6
C ₁₄ H ₂₉ N(CH ₃) ₃ Cl	67.5	1029.1	1.8
C ₁₆ H ₃₃ N(CH ₃) ₃ Cl	77.3	1178.6	2.0
C ₁₈ H ₃₇ N(CH ₃) ₃ Cl	86.5	1318.8	2.3

$$\text{c) } w = \frac{\rho(\text{surfac.}) \cdot V(\text{pore})}{m(\text{SiO}_2) + \rho(\text{surfac.}) \cdot V(\text{pore})} \rightarrow \frac{V(\text{pore})}{m(\text{SiO}_2)} = \frac{w}{\rho(\text{surfac.}) \cdot (1-w)} \quad \text{(I)}$$

$$A_{sp} = \frac{2\pi r l}{m(\text{SiO}_2)} \rightarrow m(\text{SiO}_2) = \frac{2\pi r l}{A_{sp}} \quad \text{(II)}$$

$$\frac{V(\text{pore})}{m(\text{SiO}_2)} = \frac{\pi r^2 l}{m(\text{SiO}_2)} \quad \text{and with (II)} \quad \frac{V(\text{pore})}{m(\text{SiO}_2)} = \frac{A_{sp} r}{2} \quad \text{(III)}$$

$$\text{(I) - (III)} \quad r = \frac{2w}{\rho(\text{surfac.}) \cdot (1-w) \cdot A_{sp}}, \text{ values see table above.}$$

(Note: X-ray scattering is still necessary to detect the hexagonal structure.)

Solution problem 35: Preparation and volumetric determination of strontium peroxide octahydrate

- 35.1 From experiment
- 35.2 From experiment, 1 mL of 0.02 mol L⁻¹ KMnO₄ solution corresponds to 1.701 mg of H₂O₂
- 35.3 From experiment, 1 mL of 0.02 mol L⁻¹ KMnO₄ solution corresponds to 6.031 mg of SrO₂
- 35.4 From experiment, 1 mL of 0.1 mol L⁻¹ Na₂EDTA solution corresponds to 12.062 mg of SrO₂
- 35.5 $\text{SrCl}_2 + \text{H}_2\text{O}_2 + 2 \text{NH}_3 \longrightarrow \text{SrO}_2 + 2 \text{NH}_4\text{Cl}$
- 35.6 $2 \text{MnO}_4^- + 5 \text{H}_2\text{O}_2 + 6 \text{H}^+ \longrightarrow 2 \text{Mn}^{2+} + 5 \text{O}_2 + 8 \text{H}_2\text{O}$
- 35.7 Manganese(II) cations act as a catalyst.

Solution problem 36: Preparation and iodometric determination of potassium iodate

- 36.1 From experiment
- 36.2 From experiment, 1 mL of 0.1 mol L⁻¹ Na₂S₂O₃ solution corresponds to 3.576 mg of KIO₃
- 36.3 $\text{IO}_3^- + 5 \text{I}^- + 6 \text{H}^+ \longrightarrow 3 \text{I}_2 + 3 \text{H}_2\text{O}$
- 36.4 It is a comproportionation reaction
- 36.5 In a basic solution, tetrathionate dianions are oxidized to sulfate dianions
- 36.6 Oxidising ability increases from fluorine to iodine, because the ionization energy and electron affinity decrease and the ionic radii increase in this direction.
- 36.7 a) After adding an excess of potassium iodide, iron(III) cations can be titrated directly with sodium thiosulfate solution, because an equivalent amount of iodine is produced.
- $\text{Fe}^{3+} + 2 \text{I}^- \longrightarrow 2 \text{Fe}^{2+} + \text{I}_2$
- b) $\text{Cu}^{2+} + 2 \text{I}^- \longrightarrow \text{CuI} + \frac{1}{2} \text{I}_2$
- c) A well defined excess of iodine solution must be added for the titration of sulfide. The unreacted iodine is subsequently titrated with thiosulfate solution (back titration).
- $\text{S}^{2-} + \text{I}_2 \longrightarrow \frac{1}{8} \text{S}_8 + 2 \text{I}^-$

Solution problem 37: Qualitative analysis of anions in an unknown solution

- 37.1 From experiment
- 37.2 $\text{NO}_3^- + 3 \text{Fe}^{2+} + 4 \text{H}^+ \longrightarrow 3 \text{Fe}^{3+} + \text{NO} + 2 \text{H}_2\text{O}$
 $\text{NO} + [\text{Fe}(\text{H}_2\text{O})_6]^{2+} \longrightarrow [\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]^{2+} + \text{H}_2\text{O}$
- 37.3 The hydroxide anions produced during the formation of the nitrosyl complex are removed by sulfuric acid. This is the reason why the equilibrium is shifted towards the right side of the equation.
- 37.4 $5 \text{C}_2\text{O}_4^{2-} + 2 \text{MnO}_4^- + 16 \text{H}^+ \longrightarrow 2 \text{Mn}^{2+} + 10 \text{CO}_2 + 8 \text{H}_2\text{O}$
- 37.5 $\text{ClO}_4^- + 8 \text{Fe}(\text{OH})_2 + 4 \text{H}_2\text{O} \longrightarrow \text{Cl}^- + 8 \text{Fe}(\text{OH})_3$

Solution problem 38: Recycling of polymethylmethacrylate

38.1 From experiment

38.2 30 g polymethylmethacrylate = 30 g methyl methacrylate ($M = 100 \text{ g mol}^{-1}$)
theoretical yield: 30 g (0.3 mol) methyl methacrylate.

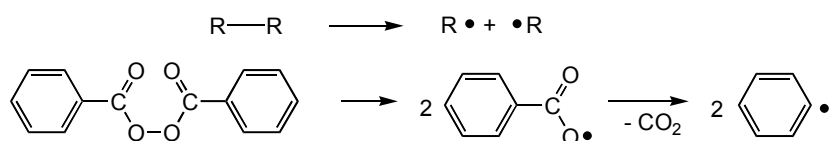
38.3 From experiment

38.4 Refractive index of methyl methacrylate: $n_D = 1.4142$.

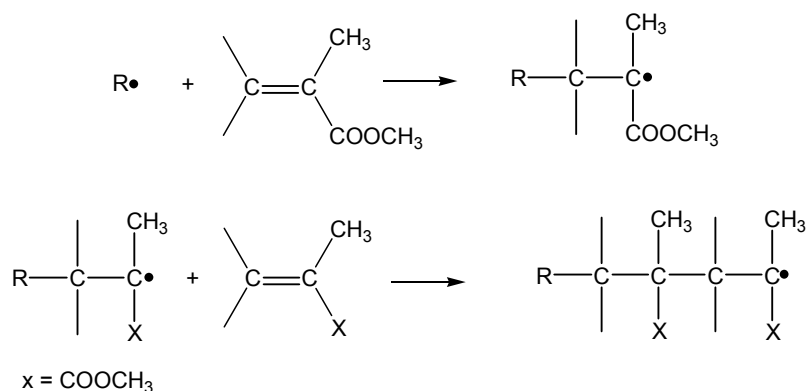
38.5 Boiling point of methyl methacrylate: b.p. = 100 – 101 °C.

38.6 Polymerization reaction of methyl methacrylate:

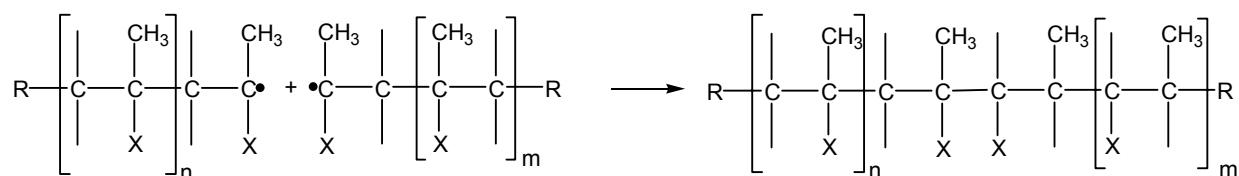
1. Initial step: decomposition dibenzoylperoxide



2. Chain initiation and chain extension:



3. Chain termination (other chain terminations are possible):



Solution problem 39: Synthesis of *para*-chlorobenzyl alcohol – an example of the Cannizzaro Reaction

39.1 From experiment.

39.2 Colorless needles from water.

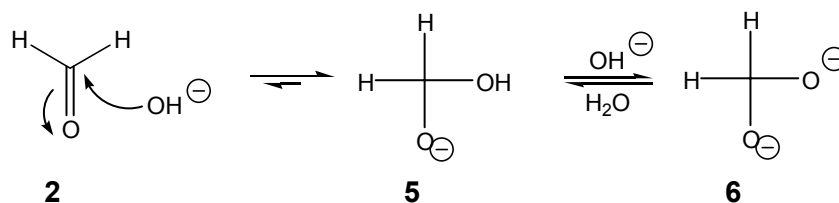
39.3 Melting point of *para*-chlorobenzylalcohol: m.p. = 75°C.

39.4 From experiment.

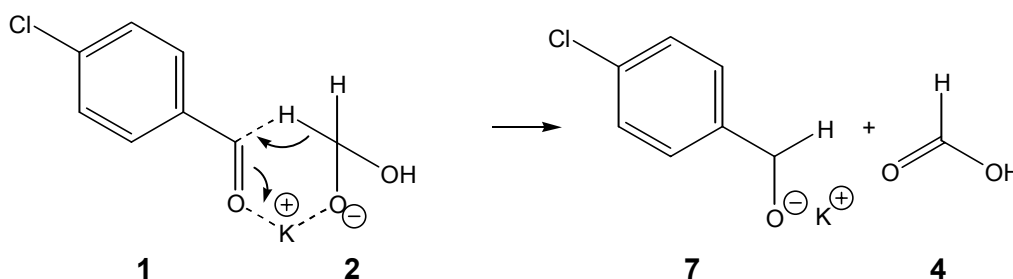
39.5 From experiment.

39.6 Reaction mechanism:

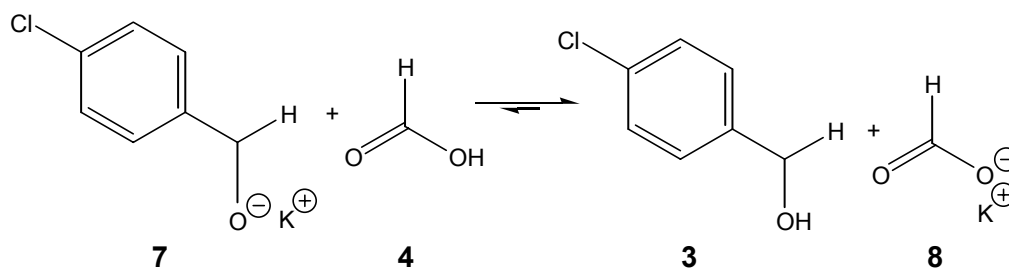
The mechanism of the Cannizzaro reaction involves a hydride (H^-) shift. In the first step a hydroxidion (OH^-) of the strong base adds to the formaldehyde **2** to give the tetrahedral anion **5**, which may lose a proton in the strong basic reaction mixture to give the dianion **6**.



The strong electron-donating character of the negative charged oxygen of **5** or much stronger in **6** forces the hydrogen to leave the anion or the dianion with its electron pair. This hydride transfer takes place, when **5** (or **6**) attacks an other molecule, which acts as a hydride acceptor, and runs through a cyclic transition state.



The final step is a rapid proton transfer from the acid **4** to alcoholat **7**.



Solution problem 40: Ammonolysis of an activated carbonic acid ester: synthesis of cyano acetamide

40.1 From experiment.

40.2 32.0 mL (0.301 mol) of cyanoacetic acid ethyl ester ($\rho = 1.065 \text{ g mL}^{-1}$, $M = 113.1 \text{ g mol}^{-1}$) = 25.3 g (0.301 mol) of cyano acetamid ($M = 84.1 \text{ g mol}^{-1}$).

40.3 From experiment.

40.4 Melting point of cyano acetamid: m.p. = 121–122°C.

Avoiding culture shock or The German way of life

People of different countries have different ways of doing things. So, to avoid culture shock, it's important to be prepared before you visit another country. Here are some notes students made after their year in Germany. This list is supposed to help you while you stay in Germany.

- Germans close room doors and pull shades.
- They worry about their health. (There's something wrong with them if they don't.)
- They get up early – and go to bed early.
- They have small refrigerators. (You shouldn't raid them.)
- There is more fresh food, less processed stuff.
- Meals are social events (so hold back with your fork until everybody is there.)
- If guests want more food, they take it. (Don't wait to be asked or you'll wait for ever.)
- Germans absolutely love mineral water.
- They would never visit other people's home without an invitation.
- They bring flowers when they visit friends. (Uneven number, no red or white roses unless in love.)
- They shake hands any time they meet people.
- They don't stand in line. (You have to push your way to the front of stores and onto trains.)
- Few people use credit cards for shopping.
- There are often restroom attendants. (They expect money.)
- Weekends are totally dead.
- German families go for long walks on Sundays.
- Germans don't waste time on polite phrases – they say what they mean.

- Page 5 (periodic table): Symbol for radium Ra instead of Rd.
- Page 26 (Problem 17.5): L-Val instead of L-Va.
- File Prep.Prob. 8/8: Page numbers 55 to 61 instead of 39 to 45.